THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR

Thesis Presented for the Degree of Doctor of Philosophy

by

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CONTENTS.

INTRODUCTION.

It has long been realised that chemical reactions can be classified in two categories - homogeneous and heterogeneous. The former occur entirely in the gas, or liquid, phase, while the latter occur partly at surfaces - such as the surface of the containing vessel, or the surface of dust particles - and degenerate into surface reactions when the fraction occurring in the gas phase becomes negligible. Thus the two may be easily distinguished by altering the area of the surface without changing the material or volume of the vessel; if the reaction velocity remains the same, the reaction is homogeneous, whereas if the rate is appreciably altered it is heterogeneous. In addition, heterogeneous reactions are especially sensitive to catalysts, or contact agents.

The fact that the decomposition of hydrogen peroxide is sensitive to catalysts has been known practically since its discovery by Thénard in 1818[1]. From that time onwards the study of the properties and reactions of hydrogen peroxide has aroused the interest of many chemists, this being due in no small measure to its inherent instability, in that it decomposes into water and oxygen with great ease, even

at/

at ordinary temperatures. This property, indeed, renders it no less interesting to the organic chemist than it is to the physical chemist, as it can profitably be used in oxidation reactions for two reasons: (a) it is more reactive than free oxygen, 23.1 k.cals. per gm. mol. being evolved in its decomposition; (b) it leaves behind only the common substance water, which is frequently present in any case. It is little wonder, therefore, that no year passes but several papers concerning various aspects of the chemistry of hydrogen peroxide appear in the annals of chemistry.

In recent years much work has been done on the kinetics of the decomposition of aqueous solutions of hydrogen peroxide, mainly in the presence of catalysts such as metals, alkalis, and light, but, even so, many problems still remain unsolved. The general trend during the last thirty years, or so, appears to be towards the use of more concentrated and chemically purer solutions. It should be mentioned, in passing, that the commercial product normally contains some negative catalyst (such as acetanilide) to inhibit decomposition and ensure a longer storage life. It is thus useless for quantitative work. Early investigators used weak solutions, as the instability of the peroxide made the production and manipulation of concentrated solutions exceedingly difficult. During the/

the last few years, however, a few excellent methods for the preparation of chemically pure concentrated solutions, and even 100% H_2O_2, have appeared in the literature.[2,3,4].

While the decomposition of hydrogen peroxide in solution has been investigated by many workers (vide infra), so far as can be ascertained only two papers and one note have been published dealing with the thermal decomposition of the vapour. This is surprising in view of the wide-spread occurrence of H_2O_2 in many reactions of which the kinetics have not been fully established, and the fact that a vapour presents a simpler medium for investigation than does a solution, on account of the absence of many complicating factors, such as solvation and ionisation. Furthermore, the workers who have investigated the decomposition of the vapour have not corroborated one another's results - the only point on which all are agreed is that the reaction is heterogeneous - and none have employed greater concentrations than 70% H_2O_2. It can be seen therefore, that an investigation into the thermal decomposition of hydrogen peroxide under conditions of the greatest simplicity is overdue, and the present investigation was designed to fill that gap.

Historical./

Historical.

As already mentioned, hydrogen peroxide was discovered by Thénard in 1818[1], the mode of preparation being the action of dilute sulphuric acid on barium peroxide. It is also interesting to note that he was the first to investigate its catalytic decomposition[5]. From that time, innumerable papers on the preparation, constitution, properties and reactions of hydrogen peroxide have appeared in the literature, so it would be almost impossible to give a full account of its history. Several interesting points may, however, be mentioned.

Thénard gave his newly discovered substance the name of "eau oxygenée", which seems to be particularly apt in view of its properties. Its formula up till 1860 was given as HO_2 [6] (water being HO); in 1865 it is quoted as "HO or H_2O_2" [7]; while by 1872 it had become established as H_2O_2. [8] An interesting series of papers dealing with the chemistry and occurrence of hydrogen peroxide was published in the years around 1880 by Schöne, Berthelot and Leeds. The subjects investigated by these authors included (a) the occurrence of hydrogen peroxide in rain water[9]; (b) the mutual decomposition of ozone and hydrogen peroxide[10]; (c) the mechanism of the decomposition of H_2O_2 in the presence of alkalis[11]; (d) the electrolysis of H_2O_2 [12]; (e)/

(e) the decomposition of aqueous solutions of H_2O_2 [13].
For the estimation of hydrogen peroxide, Schöne developed the well-known permanganate titration, which reaction had previously been investigated by Brodie[14], but was now shown to be the most convenient method for quantitative work. In addition to this work Schöne also wrote a brochure in Russian entitled "Experimental Investigations on Hydrogen Peroxide" (Moscow, 1875). The last subject mentioned above (the decomposition of aqueous solutions of H_2O_2) especially, has been the basis of a great amount of research work from that time to the present day and, although a satisfactory explanation for one aspect has recently been suggested by Rice[15] many outstanding problems still remain. A short account of the recent work in this field will be given below.

Watt's' "Dictionary of Chemistry" (1865)[7], quoting Thénard, stated that sunlight has no effect on the decomposition of hydrogen peroxide. However, it has since been well established that the decomposition is accelerated by light - e.g. Mellor[16] states that "a solution of hydrogen peroxide decomposes when it is exposed in a quartz vessel to the rays of light from a mercury vapour lamp [and] the decomposition ceases when light is extinguished". The mechanism of this decomposition has received much attention, the most

important/

important recent papers published on the subject being by Rice[15], Urey, Dawsey and Rice[17], Allmand and Style[18], Heidt[19], and Kornfeld[20, 21]. It would appear that Kornfeld[21], in her later investigation (1935) has been able to correlate the mechanism of the photodecomposition with that proposed by Haber and Weiss[22] for the decomposition in the presence of iron salts, but in view of Rice's experiments on the effect of dust particles on the decomposition[15] it is doubtful how much reliance should be placed on her interpretation. These mechanisms for the decomposition of hydrogen peroxide assume that the peroxide first decomposes into two OH radicals - as might be supposed from its constitution (vide infra). This led, in 1942, to an attempt, by Blaedel, Ogg and Leighton,[23] to detect free hydroxyl as an intermediate in several photochemical reactions. A spectroscopic method utilising the absorption spectrum of hydroxyl was used, but no free hydroxyl was detected under their experimental conditions. From their results, these workers calculated that the steady-state concentration of hydroxyl, if any, was less than 5×10^{-5} mm. The position at present is thus rather unsatisfactory.

The catalytic decomposition of hydrogen peroxide was first observed by Thénard[5], soon after its discovery. Indeed, the reaction which he used for the estimation/

estimation of the strengths of peroxide solutions was the catalytic decomposition by means of blood fibrin[14b]. It would be impossible here to give even a summary of the huge volume of work which has been published on this subject (some remarks on recent work are appended in a later section), but two interesting phenomena are worth recording.

(1) In 1903 it was observed by Bredig and Weinmayr[24a] that, if hydrogen peroxide is allowed to decompose catalytically at a mercury surface and samples are titrated at regular intervals of time with potassium permanganate solution, the resulting titration curve is sinuous. The same 'periodic decomposition' was noticed when other substances, such as iodine and colloidal metals, were used as catalysts and is exhaustively dealt with by Hedges and Myers in their book on "Physico-chemical Periodicity".[24b]

(2) In 1922 another peculiar effect was observed by Schwarz and Friedrich,[25a] who found that, if a peroxide solution decomposing at a platinum black surface was irradiated by X-rays - or even if the platinum black was exposed to X-rays before immersing it in the solution - a considerable retardation from the normal rate of decomposition was effected. The decomposition, in this case, followed the bimolecular law.[25b]

Many/

Many methods of preparation of dilute solutions of hydrogen peroxide have long been known, but only within recent years has it been possible to prepare the pure anhydrous substance. The difficulty has lain in the fact that it is impossible to distil its solutions, even in vacuo, without a certain amount of decomposition occurring. In consequence, the physical properties and physical constants of pure H_2O_2 could not be determined with any accuracy. However, this gap in our knowledge has now been filled, mainly on account of the excellent work of Maass and his collaborators in America,[26] and the properties of pure peroxide are now accurately known. The history of the determination of the structure of hydrogen peroxide is described in a later section.

Only three papers dealing with the thermal decomposition of hydrogen peroxide vapour have been traced in the literature. In 1923 part of a paper by Hinshelwood and Prichard[27] was devoted to the subject, while a more detailed study was undertaken in 1927 by Elder and Rideal.[28] The most recent - a short note commenting on several aspects of the latter's results in the light of their own investigation - was published by Kistiakowsky and Rosenberg in 1937.[29] These papers are dealt with in some detail in a later section.

Preparation of H_2O_2.

Various methods for the preparation of dilute solutions are summarised in the following list.

(1) It was discovered by Deville[30] that if moist oxygen is passed through a tube maintained at 2000° and the issuing gases rapidly cooled H_2O_2 is present in the condensate.

(2) If water is placed in a quartz vessel and exposed to the ultra-violet radiation from a mercury vapour lamp, some of it is decomposed into hydrogen and hydrogen peroxide.[31]

(3) In the electrolysis of water acidulated with sulphuric acid, hydrogen peroxide is said to be formed at the anode.[32]

(4) The formation of peroxide is also observed when electric sparks are passed through liquid water[33] or a mixture of steam and oxygen, if the gases are rapidly cooled.[34] It is also formed when a mixture of hydrogen and oxygen is exposed to a brush discharge.[35]

(5) If the flame of burning hydrogen is allowed to impinge on the surface of water cooled by ice, hydrogen peroxide may be detected in the water.[36] It is also one of the products of the hydrogen-oxygen reaction, and any mechanism proposed for this reaction must take its formation into account.[37] Its formation has frequently been observed in the slow oxidation of metals.[38]

(6)/

(6) The most common method of preparation utilises the chemical reaction between sodium or barium peroxide and a dilute acid.[1,2,3]

So far as is known, only one method whereby a peroxide of over 90% strength may be prepared in one operation has been described. In 1932 Walton and Filson[39] found that if hydrazobenzene dissolved in benzene was treated, in a bomb, with oxygen at 0°C and 370 lb. pressure per sq. in. drops of hydrogen peroxide separated from the liquid. These drops contained 94% H_2O_2 and the yield was 97% of the theoretical, which was calculated from the equation:

$$C_6H_5NH.NH.C_6H_5 + O_2 = C_6H_5.N : N.C_6H_5 + H_2O_2$$

Hydrogen peroxide is soluble in several organic solvents, in which water is insoluble, and this method and modifications of it (e.g. the work of Hurd and Puterbaugh[40]) may frequently be used for the rapid concentration of dilute solutions. If concentration is carried out in this way, however, it is possible that the resulting peroxide may contain impurities.

In 1920 a method for the preparation of pure anhydrous H_2O_2 was described by Maass and Hatcher,[2] who used a crude 3% solution obtained from barium peroxide in the usual way. This was concentrated up to 90% by distillation in vacuo, use being made of a special sulphuric acid evacuating pump, which, in addition to evacuating/

evacuating the system, also concentrated the liquid, the sulphuric acid acting as a desiccating agent. Further concentration to 100% was effected by fractional crystallisation.

A rather less laborious method which gave higher yields, but not quite such a high concentration, was evolved by Kilpatrick, Reiff, and Rice,[3] who employed a crude solution obtained from sodium peroxide and 20% sulphuric acid. This solution was distilled in vacuo, the distillate being collected in two receivers in series, the second of which was cooled to a lower temperature than the first. The more concentrated peroxide solution collects in the first receiver, that in the second receiver being very weak. After distilling over silver sulphate to remove any chloride present, the more concentrated fraction was further concentrated by standing in a vacuum desiccator over concentrated sulphuric acid. In this way 88% H_2O_2 was obtained with but little loss by decomposition. A modification of this method was used in the present research and was found to be capable of yielding 99% H_2O_2.

In 1939 a cyclic process for the preparation of pure 100% D_2O_2 was described by Fehér[4] who suggested that this method might be profitably used for the preparation of pure 100% H_2O_2 for quantitative work. The/

The method is an adaptation of the commercial process patented by Pietsch and Adolph,[41] and consists of blowing D_2O vapour through a mixture of D_2SO_4 and $K_2S_2O_8$ maintained at 70 - 90°C. The resulting mixture of D_2O and D_2O_2 is fractionally condensed and the weak solution of D_2O_2 automatically returned to the starting-point of the apparatus, whence it is again passed through the mixture. This cycle is repeated until the required amount of 100% D_2O_2 is obtained. It is suggested that if this method were used for the preparation of H_2O_2 the apparatus could be considerably simplified, as the amount of H_2O which can be utilised is unlimited while only comparatively small amounts of D_2O are available. This method of preparation would have been admirable for use in the present research, but, unfortunately, owing to war conditions, the original paper could not be consulted at the time, although it was obtained later.

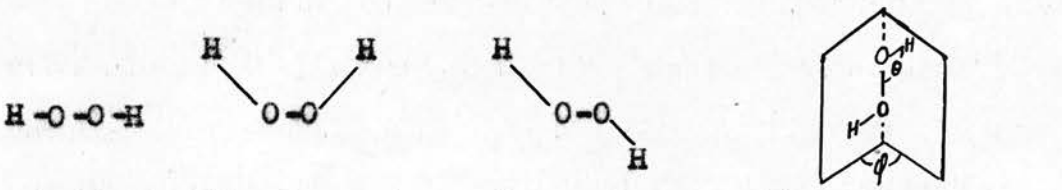
The most promising of the other methods appeared to be that of Kilpatrick, Reiff and Rice, and, indeed, with a few modifications it proved very satisfactory. Some preliminary work on this preparation was carried out in this laboratory by E. Paterson (unpublished results), on whose results several of the improvements embodied in the final apparatus were based.

Constitution.

Before any definite mechanism can be deduced for the decomposition of hydrogen peroxide it is necessary to know the constitution of the compound, for the most probable primary process depends on the structural formula assigned. This problem of the elucidation of the structure of hydrogen peroxide has aroused much speculation, and has prompted the very accurate determination of many of its physical constants. The X-ray investigation of pure solid H_2O_2, apart from the difficulties arising from its instability and low melting point ($-0.89^{\circ}C$) is, unfortunately, not conclusive, as the hydrogen atoms are too light to cause much scattering. However, the results obtained by this method in conjunction with interpretations of the values of various physical constants, such as parachor, dielectric constant and dipole moment, as well as the Raman spectrum, the infra-red spectrum, and electron diffraction photographs, have all confirmed one structure, so it may be taken that this problem is now solved.

From a consideration of its chemical properties three structural formulae have been suggested for hydrogen peroxide: (a) 'dihydroxyl' - HO-OH; (b) $\begin{matrix} H \\ H \end{matrix}\!\!>\!O \rightarrow O$; (c) a co-ordination formula $\left[H(O_2)\right] H$.[42] Formula (c) does not seem to have received much recognition, (a) and (b) being the two generally regarded as/

as probable structures, but no definite choice could be made between them from chemical evidence alone. Four configurations appear possible for (a):[43]



Straight form (a)I | Cis-form (a)II | Trans-form (a)III | Non-planar form (a)IV

Linton and Maass[44] investigated the dipole moment of hydrogen peroxide in solutions, and found that it had the valus 2.13×10^{-18} e.s.u. The molecule therefore cannot be symmetrical so that formulae (a)I and (a)III are refuted; (a)II also need not be taken into consideration, as the dipole moment of this configuration would be very small. Linton and Maass therefore favoured formula (b), and suggested that the parachor data[45] and dielectric constant measurements[46] supported their conclusion. Theilacker,[47] however, showed that the same data could be equally well accounted for by the dihydroxyl formula if it were assumed that the OH groups were free to rotate round the O-O bond. The question thus remained open, the data then available not being sufficient to decide in favour of either of the formulae (a) or (b).

Eventually, in 1934, Penney and Sutherland,[48] on the basis of quantum mechanical calculations, found that structure/

structure (a)IV, in which θ (the angle between the hydrogen atoms and the O-O bond) and φ (the azimuthal angle) are both about 100°, was the most probable as it would be about 10,000 cals. more stable than (a)II or (a)III. The dipole moment calculated for this structure agreed with that observed by Linton and Maass[44] and this configuration also accounted for the Raman lines observed by Venkateswaran[49] and Simon and Fehér,[50] which could not be explained on the basis of formula (b). Fehér[43] later made a comparison of the Raman spectra of pure H_2O_2, HDO_2, and pure D_2O_2 and came to the conclusion that his results could only be explained by a structure of the type (a)IV in which θ and φ were in the region of 90°.

Fehér and Klötzer[51a] were the first to attempt a determination of the structure of crystalline H_2O_2 by the X-ray method. They found that the crystals had D_{4h} Laue symmetry and contained four molecules per unit cell, which had the dimensions: a = 4.02; c = 8.02 Å. These figures were also obtained by Natta and Rigamonti[51b], but they thought the most probable space group was D_4^3 or D_4^4; the only other information which they could derive from their measurements was that it was probable that the four atoms of the molecule were not co-planar.

An X-ray investigation into the structure of liquid H_2O_2 was performed, in 1937, by Randall[52] who showed/

showed that his results were in accordance with the structure assigned by Penney and Sutherland, but suggested that the angles θ and ϕ were probably nearer 90° than 100°. In 1941 an X-ray determination of the structure of H_2O_2 in "hyperol" ($CO(NH_2)_2.H_2O_2$), an addition compound with urea, was carried out by Lu, Hughes and Giguère,[53] The structure of this compound was determined in the usual way, and it was found that the urea molecule had the same configuration, to within experimental error, as in the urea crystal. Assuming that the two hydrogen atoms of the hydrogen peroxide molecule lay on the two hydrogen bonds by which it was linked to the urea molecule, they were able to determine the structure of hydrogen peroxide. When this structure was worked out it was found to correspond to that proposed, from quantum mechanical considerations, by Penney and Sutherland ((a)IV above), the angle θ being 101.5° and the angle ϕ 106°, which is in very good agreement with the values suggested by the proposers ($\theta \simeq \phi = 100^{\circ}$); and in fairly good agreement with Fehér's values derived from the Raman spectra[43] and with Randall's values suggested from his X-ray study of the liquid.[52] ($\theta \simeq \phi = c.90^{\circ}$) The O-O bond length obtained from this investigation (1.46 ± 0.03 Å.) is in excellent agreement with that obtained from electron diffraction measurements carried out by Giguère/

Giguère and Schomaker,[54] which gave the O-O bond the length 1.48 Å. Zumwalt and Giguère[55] also investigated the infra-red spectrum of hydrogen peroxide vapour. Their results gave a value for the O-O bond which was in close agreement with the above, and, in addition, excluded the possibility of the peroxide being present in either the cis-((a)II) or trans-forms ((a)III).

It can thus be seen that all the evidence, most of which has been obtained during the last decade, confirms Penney and Sutherland's model for the configuration of the hydrogen peroxide molecule. This structure with all the relevant information is depicted in Figure I.

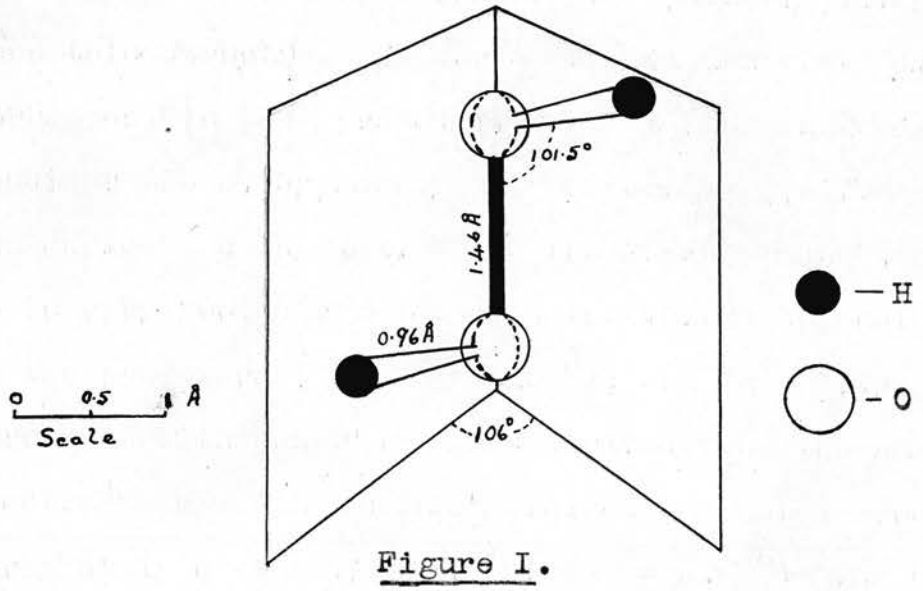


Figure I.

It has been objected[42] that it is not easy to explain the formation of H_2O_2 in the burning of hydrogen by the 'dihydroxyl' formula, (a), which, as has been described, is the accepted configuration. This/

This difficulty, however, might be fairly easily obviated on the basis of the results of Geib and Harteck (1932).[56] By the action of hydrogen atoms on molecular oxygen at the temperature of liquid air, they obtained an allotropic form of hydrogen peroxide. This form was stable only below -115°C, at which temperature it changed, with decomposition, into the form stable at ordinary temperatures. To the modification stable at low temperatures they assigned the formula $\begin{matrix}H\\H\end{matrix}\!\!>\!O\!:\!O$ (i.e. formula (b) above). They state that 'this seems likely, in so far as an addition of two H-atoms to O_2 with preservation of the double bond constitutes only a mild chemical attack,' and this is supported by Penney and Sutherland,[48] who find, by calculation, that this configuration represents a very unstable form. Thus, it seems probable that, in the burning of hydrogen, the modification originally obtained is $\begin{matrix}H\\H\end{matrix}\!\!>\!O\!:\!O$, but this, being unstable at the temperature at which it is formed, would immediately revert to the type stable at ordinary temperatures ((a)IV).

With regard to the question of resonance occurring between two or more of the possible structures, little can be said, except that Fehér,[43] on analysis of his Raman spectra, postulates a resonance degradation. The infra-red spectrum, however, gives a type of band which is characteristic of a 'spindle-shaped symmetrical top/

top molecule that is fairly rigid [and in which] the complete rotation of the OH groups about the O-O bond must be strongly hindered. A very different band structure would appear if there were a free or weakly hindered rotation'.[55]

Decomposition in Aqueous Solution.

Hydrogen peroxide is known to be formed in many systems of which the kinetics have not been fully established, e.g., the combination of hydrogen and oxygen, the photo-reaction between hydrogen, chlorine and oxygen, and generally those systems in which hydrogen atoms are produced in an atmosphere of oxygen.[56,57] For this reason the kinetics of the decomposition of hydrogen peroxide in the vapour phase is of great importance, but, in spite of this, most attention so far has been concentrated on aqueous solutions, the decomposition of which by light, heat and catalysts has been fairly fully investigated. For purposes of comparison a brief account of the work done on each of these branches is given below.

An excellent summary of the work done, up to 1928, on the photo-chemical decomposition of hydrogen peroxide is given by Kistiakowsky in his book - "Photochemical Processes".[58] However, much doubt has recently been cast on the earlier work by Rice's investigation(1926) of/

of the effect of dust particles on the decomposition.[15] Rice found that the rate of decomposition in a "dust-free" solution (prepared by distillation in vacuo without ebullition) in the light of a mercury vapour lamp was very much less than that in a solution prepared in the normal way, and suggested that the ratio of the rates should be 1:100, in which case the quantum yield in the "dust-free" solution would be unity. Therefore, a chain reaction would be unnecessary for the explanation of the decomposition, the high quantum yields obtained by other workers (e.g. Kornfeld[59] found a quantum yield of 80 for a 2% solution, while Allmand and Style[18] observed later that the quantum yield varied between 500 and 20 with increase in the intensity of the light) being due to the decomposition of aggregates of H_2O_2 molecules on the dust particles. Heidt[19] verified the fact that, with "dust-free" solutions and high intensities, the quantum yield approaches unity (this, incidentally, also substantiates the predictions of Griffith and McKeown[60] for high intensities), while Rice and Kilpatrick[61] have also confirmed the theory by finding that the rate of photo-decomposition was proportional to the dust content of the solution.

Kornfeld,[21] however, maintains that the effect of dust particles is only appreciable in concentrated solutions and has attempted to correlate the mechanism for/

for the photo-decomposition of dilute solutions (less than 1%) with that proposed by Haber and Weiss[22] for the catalytic decomposition by iron salts. This view does not appear to be valid, however, as Rice found that if two quartz flasks containing 2% solutions, one of which was dust-free, were placed near a mercury vapour lamp, the ordinary H_2O_2 solution appeared to boil while the effect of the light on the other was unnoticeable. Urey, Dawsey and Rice,[17] in the hope of obtaining some evidence with regard to the process occurring on absorption of light, investigated the absorption spectrum of hydrogen peroxide and its vapour, but their results were ambiguous. The energy of the longest wavelengths absorbed was sufficient to cause any of the following:

$H_2O_2 + h\nu = 2OH$: $H_2O_2 + h\nu = HO_2 + H$; $H_2O_2 + h\nu = H_2O + O$.

They favoured the first of these three reactions, and, as the water bands (due to OH) appeared in fluorescence when the zinc spark lines from 2025 - 2138 Å were used for illumination, they concluded that the reaction occurring under these conditions was:

$$H_2O_2 + h\nu = OH\ (^2P) + OH\ (^2S):$$

However, for illumination with light of wavelengths between 2200 and 3000 Å they considered the most likely process to be:

$$H_2O_2 + h\nu = OH\ (^2P_{1/2}) + OH\ (^2P_{3/2}),$$

which/

which would be analogous to the primary processes occurring when the halogens absorb light in the continuous region of their spectra. They do not, as stated by Heidt,[19] favour the process:

$$H_2O_2 + h\nu = H_2O + O.$$

The decomposition of the peroxide into two OH groups is the one which appears most probable from the constitution of H_2O_2 (see above), but, although Blaedel, Ogg and Leighton[23] attempted to obtain direct spectroscopic evidence of the presence of OH as an intermediate in several photochemical reactions, including the photodecomposition of H_2O_2, no free hydroxyl was detected. If it were present, therefore, it must be at a pressure of less than 5×10^{-5}mm. The question of the mechanism of the photochemical decomposition of hydrogen peroxide is thus by no means completely solved, but the evidence seems to favour Rice's view that dust particles play an important part and full elucidation of the mechanism can only be obtained by using dust-free solutions.

The work on the catalytic decomposition of hydrogen peroxide can be divided into two parts - homogeneous and heterogeneous catalysis. As heterogeneous catalysis will be considered under the thermal decomposition, here we need deal only briefly with catalysis by dissolved substances - such as alkalis, acids and metallic salts. Pana[62] has shown that alkalis, such as/

as sodium hydroxide, do have a definite catalytic effect on the decomposition, which cannot be accounted for on the assumption that the alkali contains small amounts of iron salts. The effect of alkalis and acids has also been studied by Wright and Rideal,[63] who found that the greatest rate of decomposition occurred at a pH corresponding to the iso-electric point for the surface, where, as H_2O_2 is practically a non-electrolyte, the adsorption would be greatest. This effect thus appears to be due to a surface reaction. In 1934 an important paper on the catalytic decomposition by iron salts was published by Haber and Weiss,[22] who proposed a mechanism, which, they claim, explains the results obtained and also some peculiarities which have been observed. Here again the primary process is the decomposition of the H_2O_2 into two hydroxyl groups, one of which is, however, ionic, as it has taken one electron from the ferrous ion - i.e.,

$$Fe^{\cdot\cdot} + H_2O_2 = Fe^{\cdot\cdot\cdot} + OH' + OH.$$

They also assume that either a chain or radical mechanism is possible. Jeu and Alyea[64] performed an interesting series of experiments on the effect of dissolved negative catalysts on the photo-decomposition of H_2O_2. To interpret their results they employed the following equation derived from the unimolecular law:/

law:

$$\frac{dx}{dt} = \frac{K(1 - x)}{k_2 + kC}$$

where dx is the fraction reacting in the time interval dt: x is the fraction decomposed in time t: C is the concentration of inhibitor: K, k, k_2 are constants. In the derivation of this expression the chain is assumed to be of some considerable length, which seems inadmissable from the point of view of Rice's theory. The expression itself however is interesting from the point of view of the results obtained in the present work.

The thermal decomposition, with which we are more concerned, has also merited much consideration. Two exhaustive papers on the subject were published in 1914 and 1915 by Lemoine[65] and Clayton,[66] respectively. Both these authors used peroxide containing inhibitors but several of their observations which have since been further developed may be mentioned. In the interpretation of their results they both use the unimolecular rate equation, although Lemoine's unimolecular constant is very variable. Lemoine observed that unfiltered air passed through the solution hastened the decomposition, while with filtered air the increase in rate was very much smaller - again demonstrating the importance of dust particles. He also noted the effect of surface on the reaction, and made the observation/

observation that strong solutions were much more stable than weak solutions, deducing from this that water acted as a catalyst. It has been suggested, however, that what really happens is that concentrated H_2O_2 solutions have the power of destroying active surfaces for decomposition (e.g. of dust particles) and that this destruction accounts for the increased stability.

The results of Clayton[66] indicate that the purity of the water employed has a great effect on the rate of decomposition. In some of his experiments he employed water from which organic matter in the colloidal state had been removed by distillation through a red-hot quartz spiral, and found that, in this case, the rate of decomposition was considerably reduced. He makes the statement that purity of the solvent has probably more effect on the rate of decomposition than the walls of the vessel. This again indicates the supreme importance of employing dust-free solutions. The next important advance in the study of the thermal decomposition of hydrogen peroxide came, in 1926, with the publication by Rice of his classical paper on the effect of dust particles.[15] In this paper he makes the interesting observation that the thermal decomposition is almost entirely suppressed if the reaction is carried out in dust-free solution and in a freshly fused vessel, while if a glass surface is roughened - e.g. by hot cleaning solutions - it becomes very active catalytically/

catalytically. In the next year Rice and Reiff[67] demonstrated that with dust-free solutions a zero order reaction is obtained, whereas, if tap-water was used to make up the solution, the reaction approximates to a unimolecular one. Both these effects have since been corroborated by Williams,[68] who suggests, in addition, that a silica surface has a number of preformed "active points" at which decomposition occurs, while on a glass surface the H_2O_2 itself creates centres of activity.

Silica gel has been shown to have only a slight catalytic effect on the thermal decomposition, but this activity is greatly enhanced by impurities.[69] A possible explanation of this is furnished by the results of Wright and Rideal[63] quoted above.(page 23)

A series of experiments on the heterogeneous decomposition of H_2O_2 in heavy water has been described by Giguère and Maass,[70] who found the reaction to be unimolecular. From their results, they suggest that D_2O_2 is more stable towards catalysts than H_2O_2. No special precautions to prevent the access of dust appear to have been taken.

The results on the thermal decomposition of aqueous solutions of hydrogen peroxide may be summarised as follows:

(1) The rate of decomposition depends mainly on the dust particles and colloidal organic matter present in the solution.

(2)/

(2) It also depends on the state of the surface.

(3) In the absence of dust particles and at a freshly fused surface decomposition practically ceases.

(4) In dust-free solutions the reaction is of zero order.

(5) In normal "dusty" solutions the rate of decomposition approximates to unimolecular order.

(6) A silica surface appears to have a number of preformed "active points" for decomposition, while the peroxide creates its own "active points" at a glass surface.

(7) The greatest amount of decomposition occurs in solutions of pH coincident with that required to bring the surface (e.g. of the vessel) to its iso-electric point.

Thermal Decomposition of Vapour.

In view of the extensive study of the decomposition of hydrogen peroxide in solution, it is rather surprising that so little work has been carried out in the vapour phase, in which many of the complicating factors present in the liquid phase should be eliminated. As far as can be ascertained, however, this reaction was completely neglected until 1923, when it was investigated by Hinshelwood and Prichard.[27] They employed a method whereby a known weight of 30% peroxide (Merck's perhydrol/

perhydrol) was introduced into a glass bulb, which was then immediately evacuated and sealed off. The bulb was heated to 76°C., at which temperature the quantity of peroxide introduced exerted a pressure less than the saturation pressure. The H_2O_2 immediately boiled off and the amount remaining after a certain time was estimated by breaking the bulb under water and titrating the solution. This method suffers from the serious disadvantage that the rate of decomposition of the same sample at different times cannot be measured, a different sample having to be used for each determination. They found the reaction to proceed as a unimolecular surface reaction, although their unimolecular constant was rather variable. Glass wool introduced into the vessel caused the H_2O_2 to decompose almost immediately.

The only other investigation of which detailed results have been published was carried out by Elder and Rideal,[28] who investigated the decomposition of hydrogen peroxide vapour at surfaces of glass, quartz, platinum and mercury. The apparatus employed was a great improvement on that employed by the previous workers, as it enabled measurement of the amount of the same sample decomposed at different times, and thus cut out errors due to variation in the samples and changes on the surface of the vessel between two runs. A small measured amount of H_2O_2 (just insufficient to give/

give saturation pressure at the reaction temperature) was introduced into a Vitreosil bulb, and the system evacuated. After evacuation, a thermostat, set for 85°C, was placed round the bulb and changes in pressure at constant volume recorded at suitable time intervals by means of a liquid paraffin manometric system. The vapour, on investigation, proved to consist of simple molecules of peroxide and water, and not of molecules of a compound hydrate. No reproducible results could be obtained with glass, but quartz was found to be fairly satisfactory. In all their experiments they observed the phenomenon that the reaction came to an abrupt end when a small fraction of the hydrogen peroxide present had decomposed, and to get an 'infinity' reading (corresponding to complete decomposition) the vessel had to be heated to 300 - 400°C in a Bunsen flame. From an analysis of their results they came to the conclusion that, on quartz, the reaction is of zero order, inhibited by one of the products, which, they suggest, is oxygen. On platinum the reaction appears to be unimolecular, while at a mercury surface no trace of a periodic reaction was found - in contrast to the decomposition of a solution at a mercury surface.[24]

In 1937 Kistiakowsky and Rosenberg[29] attempted to verify these conclusions, and published a note giving results obtained with a 'pure' 70% hydrogen peroxide solution/

solution. So far as can be ascertained, no paper giving experimental data has yet been published by these workers, but they say that a static method was employed. At 85°C and 98°C the heterogeneity of the reaction was again proved - times for fifty per cent decomposition varying from one minute to thirty minutes, depending on changes in the vessel surface. In contrast to the observation of Elder and Rideal, no cessation of the reaction after a small amount had decomposed was found. Preliminary flushing out with oxygen is said to have no effect on the rate of the reaction, but no indication of the order of the reaction is given.

It has been mentioned above that hydrogen peroxide is formed in the hydrogen - oxygen reaction, and an exhaustive study of this reaction by von Elbe and Lewis[71], in 1942, led to a suggestion for the mechanism of the decomposition of hydrogen peroxide. The scheme consists of twelve probable reactions, only the first four of which we need consider here.

$$H_2O_2 + M = 2OH$$

$$OH + H_2 = H_2O + H$$

$$H + O_2 = OH + O$$

$$O + H_2 = OH + H$$

In the first equation M could be any molecule present in the gas phase, or it could represent the wall of the vessel/

vessel. Here again the decomposition into two hydroxyl radicals is considered to be the primary process, but, in this reaction at any rate, it can be seen that the same net results would be obtained if it were assumed that the peroxide decomposed into H_2O and O, although, from the constitution, this appears improbable.

Scope of the Present Investigation.

In view, therefore, of the unsatisfactory condition of our knowledge regarding the thermal decomposition of hydrogen peroxide and the importance of this reaction in many systems, the present work was designed to investigate the reaction under the simplest possible conditions, and to see whether results obtained in this way could be correlated with those of previous workers, who had used different methods and conditions.

To this end the following conditions were imposed:

(a) The decomposition of the vapour was investigated, as this should present an inherently simpler system than does a solution.

(b) The vapour employed was drawn from a very concentrated solution in order to eliminate, as far as possible, any effect of solvent on the reaction.

(c) Low pressures (≤ 1 mm.) were used to minimise any gas-phase reaction (all previous workers are agreed that/

that the reaction is heterogeneous), and also to enable employment of an all-glass pressure registering device which eliminated mercury and oil manometers and any effect these might have on the system.

The vapour actually employed in most of the experiments was taken from a 99% H_2O_2 solution which was specially prepared and which, according to the data of Giguère and Maass,[72] should give a vapour containing 91% H_2O_2. There was then investigated the influence, on the decomposition, of oxygen, pressure of H_2O_2, water vapour, inert gases - such as nitrogen, hydrogen and carbon dioxide - temperature and the presence of P_2O_5. Silica vessels were employed throughout the work as it was found by Elder and Rideal[28] that a silica surface gave the most reproducible results.

EXPERIMENTAL.

(1) PREPARATION OF HYDROGEN PEROXIDE.

As mentioned in the Introduction (page 11), the method of preparation of hydrogen peroxide employed in the present investigation was based on that of Kilpatrick, Reiff and Rice,[3] and included several modifications and improvements based on the results of preliminary experiments. However, as determinations of the concentration of hydrogen peroxide in solutions constituted a considerable part of this section of the work, an account of the method employed is inserted before the description of the actual preparation.

(a) Estimation of H_2O_2 in Solutions.

Titration with deci-normal potassium permanganate solution was employed for estimation of the hydrogen peroxide content of solutions. The potassium permanganate used was standardised by the following method, which, it is claimed,[73] gives a very accurate result. About 0.3 gm. of AnalaR sodium oxalate which had been dried at 105°C was accurately weighed into a 600 ml. pyrex beaker. 250 ml. of a solution of sulphuric acid, prepared by adding 15 ml. of A.R. concentrated sulphuric acid to 285 ml. of water, boiling for ten minutes and/

and cooling to $27^{\circ} \pm 3^{\circ}$, were added. After the oxalate had dissolved, 40 ml. of the approximately N/10 potassium permanganate were added, running in about 30 ml. per minute, while the temperature was kept at about 27°. When the pink colour had disappeared, the solution was heated to between 55° and 60°, and the potassium permanganate run in until a very faint pink colour persisted for half a minute. The last millilitre was added very slowly, the colour due to each drop being allowed to disappear before the next one was added. A blank experiment, omitting the sodium oxalate, was also carried out.

The normality of the permanganate as determined by this method was 0.1025 N.

For estimation of dilute solutions of peroxide (i.e. less than 10%) the usual procedure of direct titration with potassium permanganate was employed,[74] but when more concentrated solutions were estimated, a special procedure, worked out by E. Paterson, was adopted. A weighing bottle about half filled with distilled water was accurately weighed. 0.05 to 0.10 gm. of the H_2O_2 solution was delivered into the bottle from a pipette, the lid replaced, and the bottle again weighed. The contents of the bottle were then transferred to a 300 ml. conical flask, containing about

100/

100 ml. water and 30 ml. dilute sulphuric acid, and the weighing bottle well washed out into the flask with distilled water. The solution was made up to about 200 ml. and titrated with the deci-normal potassium permanganate solution. From the results the percentage H_2O_2 by weight in the original solution could be calculated.

(b) Preparation of a Crude Solution of H_2O_2.

The materials used in the preparation of the crude solution of hydrogen peroxide were AnalaR sodium peroxide and 20% sulphuric acid, prepared by diluting A. R. concentrated sulphuric acid with distilled water. The sodium peroxide was added in small quantities, with constant stirring, to a known volume of the acid in a large pyrex beaker cooled in a freezing mixture, until an amount equivalent to 95% of the acid had been introduced. During this process care had to be taken to prevent the temperature of the mixture exceeding $10^{\circ}C$, as, otherwise, much decomposition of the H_2O_2 occurred and the resulting solution was very weak. After standing for an hour at 0° - 5° C, the crystals of sodium sulphate decahydrate which had separated were filtered off, but, as it is reported that these sometimes retain up to 20% of the peroxide formed,[3] they were washed several times with ice-cold water. The amount of washing water/

water used was carefully chosen so that, while removing the greater part of the peroxide from the crystals, the solution would not be diluted excessively and the ensuing distillation rendered too laborious. In practice it was found that the optimum amount of washing water was approximately 200 ml. for the crystals obtained from 100 ml. sulphuric acid - an amount which was found to be the most convenient for one preparation, and which was always the quantity employed to prepare a solution for each distillation of the first type. In this manner a solution containing approximately 6% H_2O_2 was obtained.

(c) Concentration and Purification of the H_2O_2 Solution.

Apparatus.

Removal of the sodium sulphate still remaining in the solution and further concentration of the peroxide were effected in one process by distillation in vacuo. As hydrogen peroxide attacks rubber, and is thereby liable to contamination if it were to come into contact with rubber during distillation, the first attempt at this distillation was carried out in a standard "Quickfit" pyrex glass apparatus, in which all connections were made by interchangeable ground joints lubricated with Apiezon grease L. In place of the normal single receiver, two were connected in series and the apparatus was connected through a sulphuric acid trap to a McLeod/

McLeod gauge and an oil-pump. This arrangement, however, proved unsatisfactory for two reasons: (a) leaks tended to occur, which were difficult to locate on account of the large number of ground joints; (b) the smallest receivers which were obtainable (100 ml. flasks) were too large for the small amount of concentrated peroxide obtained.

To eliminate these difficulties, there was next constructed an apparatus consisting entirely of soda-glass, in which ground joints were employed only when absolutely necessary. It was found, however, that, if the condenser was placed at the conventional angle, the final fraction of the distillate - which was the most concentrated in H_2O_2 - tended to adhere in droplets to the walls of the condenser and could only be removed by passing hot water through the condenser. This caused considerable decomposition, which had to be avoided if at all possible, and it was found that the difficulty could be overcome by replacing the sloping condenser by a vertical one. The apparatus in its final form is shown in figure II.

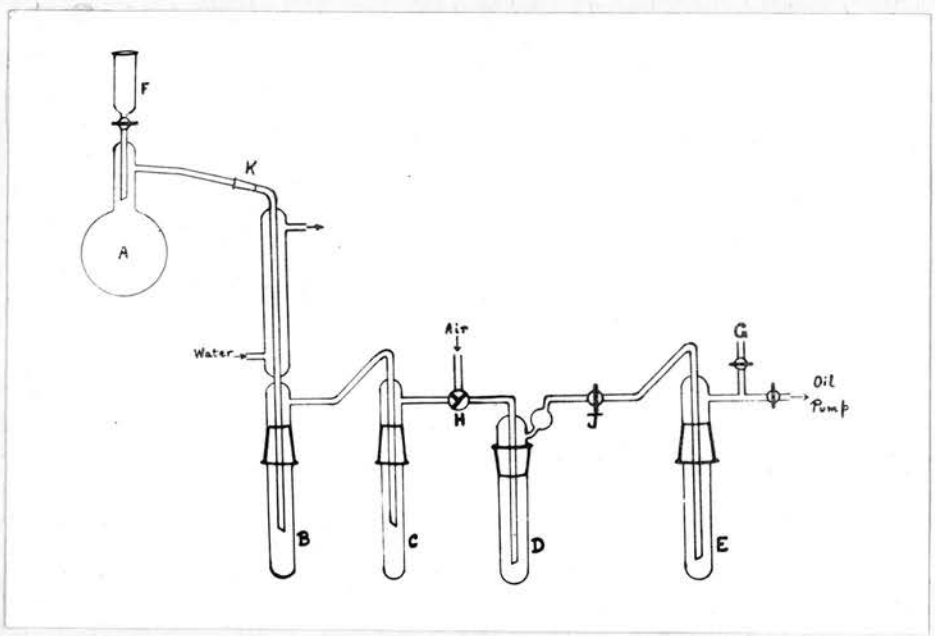


Figure II.

The delivery funnel, F, was sealed into the neck of the specially constructed distilling flask A, which was of 250 ml. capacity, and the side tube of which was connected by means of a standard interchangeable ground joint K to the top of the vertical condenser. Receivers B and C, which were of 15 and 10 ml. capacity respectively, were also connected to the apparatus by interchangeable ground joints and were duplicated, so that as little interruption as possible be made in the distillation when the receivers had to be changed. If duplicates were not available the warm liquid in A would decompose considerably when open to the atmosphere while the distillate in B and C was being melted and/

and transferred from the tubes - the distillate frequently froze in the receivers, especially in C (see below). D was a sulphuric acid trap, which, as well as acting as a desiccator for the H_2O_2 vapour, also prevented thickening of the oil of the pump,[3] and E a trap cooled in a solid CO_2-ether freezing mixture. The trap E was originally inserted because, after a distillation had been running for some time, the temperature of the sulphuric acid in D rose considerably, with the result that some vapour escaped absorption and condensed in the cool tubing further along the apparatus. As this is liable to corrode the mechanism of the pump, it had to be frozen out in E. It was later discovered, however, that, if D was cooled in ice-water and the sulphuric acid replaced a few times during the distillation, the trap E was unnecessary. Evacuation was carried out by a Cenco Hyvac oil pump and the pressure in the apparatus at any time could be determined by a MacLeod gauge connected at G. H was a three-way tap, one opening of which was open to the atmosphere, so that, in changing the receivers, the distilling part of the apparatus could be connected to the air while the vacuum in the other part remained undisturbed. All taps and joints were lubricated with Apiezon grease L.

For a second distillation, the volume of liquid

to/

to be distilled being small, the distilling flask was replaced by a specially constructed tube shown in figure III. The ground joint K was the same size as that on the side tube of the distilling flask, and fitted into the socket K at the top of the condenser (fig. II). In this case it was observed that the

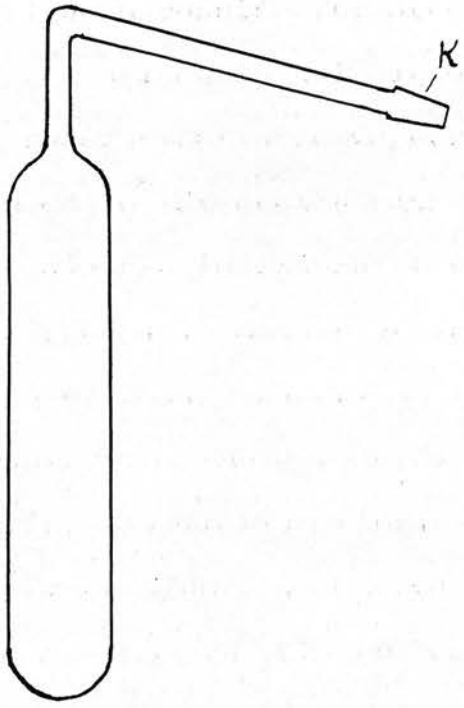


FIGURE III.

Apiezon grease, which was originally used to lubricate the joint, tended to become very fluid and flow down into the condenser, causing a leak and, possibly, some decomposition of the peroxide vapour. The joint was therefore made with Picein wax, which was found to be very satisfactory.

The/

The apparatus for the final distillation was connected to the apparatus in which the decomposition was investigated (vide infra). The first model which was employed utilised distillation into two receivers, as previously, and the vapour had to pass through greased taps during distillation. It was found, however, that the amount collecting in the second receiver was negligible and that the greased taps caused considerable decomposition, so the apparatus was simplified and the final modification is shown in figure IV.

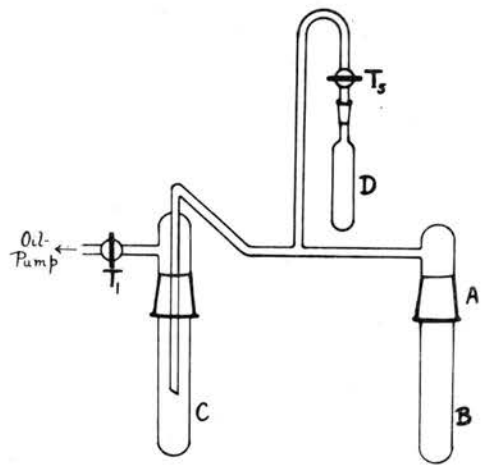


FIGURE IV.

The distilling tube B was fitted at its top with a ground joint A of the same size as that at the top of receiver/

receiver B in figure II, so that these were interchangeable. Only one receiver, C, was employed, and a sulphuric acid trap D, for concentration purposes, was attached by a T-joint to the tubing between the distilling tube and the receiver. The whole apparatus was connected to the oil-pump line of the decomposition apparatus (figure V). The joints were lubricated with Apiezon grease L, and the Cenco Hyvac pump was used for evacuation.

Experimental Procedure.

The distilling flask, receivers, and condenser (figure II) were first of all washed out with distilled water and dried by evacuation with the oil-pump. Air was then admitted to the apparatus up to the tap J. The trap D was disconnected, sufficient concentrated sulphuric acid introduced to bring the level of the acid about half an inch above the bottom of the delivery tube, and the trap replaced. D was then immersed in ice-water and the part of the apparatus between H and the oil-pump again evacuated. A large boiling-tube containing a mixture of ice and water was placed round B, while C was immersed in a freezing mixture of ice and salt (temperature about - 15°C) contained in a Dewar tube. Thus C was cooled to a lower temperature than B in accordance with the procedure of Kilpatrick,/

Kilpatrick, Reiff and Rice.[3] About 100 ml. of the crude solution were then introduced into A through the funnel F, the tap of the funnel closed and the whole system slowly evacuated. At this juncture great care had to be exercised as the liquid in the distilling flask froths and "bumps" and, if the evacuation was too rapid, some tended to "bump" over into the receivers before the actual distillation commenced. This frothing also explains why the liquid could not be run in while the whole apparatus was evacuated. On complete evacuation the frothing practically ceased, but bubbles of gas were more or less continually evolved, owing to decomposition of the peroxide. The distilling flask was then immersed in a water bath containing cold water and the water heated to 50°, at which temperature the first fraction distilled over. The pressure in the apparatus during a distillation, as measured by the McLeod gauge, was approximately 0.02 mm. Hg.

When receiver B was full, the vacuum in the distilling part of the apparatus was broken by allowing air to enter through H. The water bath surrounding A was removed, and receiver B and, if necessary, receiver C were replaced by duplicates. The amount of liquid collecting in C was normally much less than that in B, and thus it did not require replacement as often as B - usually once for every two changes in B. When the receivers/

receivers had been replaced the apparatus was again slowly evacuated and the process repeated. If the change-over of the receivers was carried out expeditiously, it was sometimes possible to re-evacuate the system without cooling the liquid in A, but frequently A had to be cooled in ice-water while the evacuation was proceeding, or the liquid would "bump" over into the receivers. In either case it was advisable to cool the water-bath to at least 25° before replacing it round the distilling flask to proceed with the distillation.

The entire distillation was performed in this way, the contents of the distilling flask being made up to approximately 100 ml. each time about 50 ml. had distilled over. The concentrated sulphuric acid in the trap D was replenished several times during the course of the distillation. When the volume of liquid in A became small and some crystals had separated in the distilling flask the temperature of the water-bath was gradually raised to keep the liquid distilling over at a reasonable rate. It was found that this gave a higher concentration than if the distillation were allowed to proceed more slowly at a lower temperature. Eventually the crystals in the distilling flask appeared dry, and at this point the receivers were changed for the last time, the temperature raised to 95 - 100° and the last fraction driven off the crystals. This fraction was found/

found to be the most concentrated in H_2O_2 - see table I (page 68) in which the concentrations of each fraction for a complete run are tabulated.

It may be mentioned here that it was found necessary to employ duplicates of the receivers in the above distillation for two reasons:

(a) The distillate frequently froze in the receivers, especially in C, and if no duplicate were available, considerable time would be lost while the distillate was being melted and transferred to another container. As indicated above, for highest concentrations, the whole distillation should be carried through as rapidly as possible.

(b) Each fraction was analysed, and, if the fraction were transferred to another container in order to replace the receivers quickly, considerable decomposition occurred on contact with the fresh surface so that the observed concentration was not that of the original fraction.

It has been reported[3] that the peroxide prepared in this way is liable to contain a trace of chloride, presumably arising from the reactants. In the present case also, a very slight trace of chloride was found to be present and was removed by distillation over silver sulphate, as recommended by Kilpatrick, Reiff and Rice.[3] As only the two final fractions collected in/

in Receiver B_A^{in} the previous distillation had any considerable concentration in H_2O_2, the four final fractions from two of the above distillations were employed in this distillation. The volume to be distilled was thus small (20-30 ml.), so the distilling flask was replaced by the tube shown in figure III and described above. Some crystals of silver sulphate were introduced into the dry tube, the hydrogen peroxide solution (which had a concentration of about 30%) added, and the tube fitted in place of the distilling flask. The distillation was carried out as before, but the receivers were cooled in solid CO_2-ether freezing mixtures, so arranged that C was at a lower temperature than B. The temperature of distillation was again raised from about 50° to 100° as the liquid became more difficult to distil. The tube was kept in the boiling water for about 5 mins. in order to drive over some of the very concentrated solution which had collected at the top of the distilling tube. As the volume to be distilled was small, the fractions collected were of a correspondingly small volume (about 2 - 3 ml.). The first few fractions were again found to be dilute (<10% - see table II), but the last two fractions collecting in B were very concentrated (the last normally being over 80%).

In order to concentrate this peroxide still further a final distillation was performed in the apparatus shown in/

in figure IV, and previously described. The apparatus was first of all washed out with distilled water and thoroughly dried by evacuation with the oil-pump. The vacuum was broken and the tube B removed. The two most concentrated fractions from the previous distillation were mixed in the receiver containing the most concentrated one, and this receiver was fitted on at the ground joint A - B in figure II and B in figure IV being interchangeable, as described above. This prevented decomposition due to transference to a new vessel. Receiver C was surrounded by a solid CO_2-ether freezing mixture, the distilling tube immersed in a water-bath, the tap to the sulphuric trap D opened, the whole system evacuated, and the distillation started. As only about 5 - 6 ml. was to be distilled, the fractions, in this case, each consisted of about 2 ml. of liquid. The optimum temperature of distillation was found to be about 60° at the beginning, the last fraction being distilled over at about 75°. As in the previous distillation the tube was immersed in boiling water for about 5 min. at the end of the distillation to heat up the tubing at the top of the delivery tube and drive over some of the concentrated peroxide which had condensed there. It was again noted that a higher concentration was obtained if the distillation were carried out quickly than if it were allowed to proceed more/

more slowly at a lower temperature. At the end of the distillation the tube from which the liquid had been distilled was replaced by a clean dry glass tube and the receiver C, which contained the last fraction, was employed as reservoir for the H_2O_2 for the ensuing experiments on the decomposition.

The results obtained in a typical distillation of this kind are given in table III (page 69), and some remarks on the preparation are appended under the heading "Discussion" (page 76).

II. DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR.

Apparatus.

The system employed for investigation of the thermal decomposition of hydrogen peroxide vapour is shown diagrammatically in figure V. The part of the apparatus to the right of tap T_1 is that depicted in figure IV, the function of which has already been described. Receiver C acted as reservoir for the concentrated peroxide, the preparation of which has been described in the previous section. Except when the H_2O_2 had to be liquefied to permit withdrawal of the vapour, this reservoir was kept immersed in a solid CO_2-ether freezing mixture in order to maintain the peroxide in the solid state and so minimise decomposition. The entire apparatus, with the exception

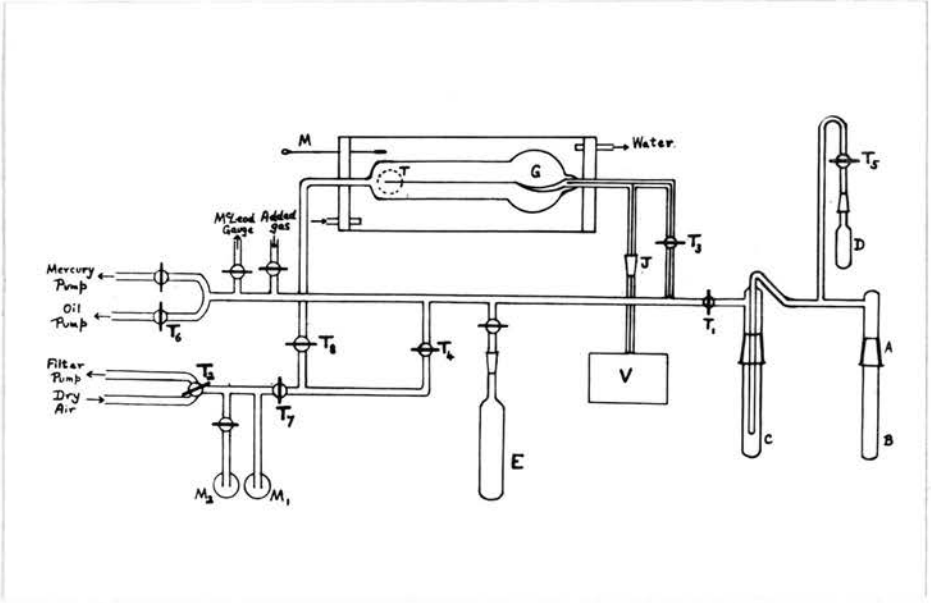


Figure V.

of the reaction vessel, was constructed of soda-glass, and all taps and ground joints were lubricated with Apiezon grease L. The quartz reaction vessel V was cylindrical in shape with optically plane ends, and was directly connected by capillary tubing and the ground joint J to the spring of the all-glass Bourdon pressure gauge G, movement of the pointer of which was observed against the eye-piece scale of a telescope T. This gauge was calibrated by introducing dry air into the vessel through the tap T_2 and noting deflections of the pointer for various pressures, as measured by the manometer M_1, read in conjunction with the standard manometer M_2. These manometers also served for measurement of pressures of gases introduced into the system when the pressures employed were in excess of those which could be read directly from the gauge. The reaction vessel employed for most of the experiments described below had a volume of 31.35 ml. and a capillary stem of 2 mm. bore: another vessel employed later was of 21.74 ml. capacity with a 1.5 mm. capillary stem.

For experiments performed in the presence of phosphorus pentoxide, a side tube with a ground joint was fused to the capillary tubing just above the joint J. The P_2O_5 was placed in a small tube which fitted on to the ground joint. As this part of the apparatus was added specially for this set of experiments, and

was removed after their completion, it is not shown in figure V.

The Bourdon gauge was maintained at a constant temperature by water syphoned from a thermostat running at a temperature of $26.4^{\circ} \pm 0.02^{\circ}C$. The temperature of the gauge jacket, as read by the thermometer M varied slightly according to the room temperature, but was kept constant to within $\pm 0.1^{\circ}$ for any one run. The maximum variation of temperature of the jacket between runs performed during the winter months and those performed during summer was 1°, and this in spite of the fact that the connecting tubing between the thermostat and the gauge was insulated with asbestos string and the jacket itself by insulating felt. It can be shown, however, that such a variation would have no appreciable effect on the calibration of the gauge at the pressures employed, so long as the temperature was kept constant for any single run.

Experiments were normally performed with the reaction vessel maintained at a temperature of approximately $80^{\circ}C$, which was effected by immersing the vessel in a thermostat running at that temperature, but for some runs at high temperatures (up to $150^{\circ}C$) the thermostat was replaced by an electric heater. The thermostat, although difficulty was originally experienced/

experienced in getting a sufficiently accurate control, was accurate to $\pm$ 0.15°, while the temperature of the electric heater was found to be easily controllable by hand adjustment of a rheostat to $\pm$ 0.3°, or less. These temperatures were registered by an accurate mercury thermometer immersed in the thermostat, or placed centrally in the furnace. The latter was constructed in two similar parts to facilitate introduction of the reaction vessel, and consisted of two heating coils wound on glass formers, the whole system, enclosed in a metal cover, being well lagged with asbestos paper and string, enabling preservation of the necessary steady temperature.

Oxygen, hydrogen and other gases were stored in glass bulb reservoirs and were introduced into the system through the tube indicated in the sketch. As a source of water vapour the tube E containing distilled water was employed. The entire system could be evacuated to a residual pressure of 0.0013 mm. Hg. by means of a filter pump and a Cenco Hyvac pump. A mercury vapour pump which, backed by the oil-pump, was used for one set of experiments reduced the pressure in the apparatus to 0.00025 mm. Hg. These pressures were recorded by a McLeod gauge.

Purification/

Purification of Gases.

All gases employed were taken from cylinders and were purified as described below, to eliminate any impurities - especially oxidising or reducing agents - which might cause undesirable effects.

Nitrogen.

The purification train for this gas is shown in figure VI. The gas was bubbled through distilled water and then passed over reduced copper gauze heated to 700°C in a pyrex tube. This treatment was employed to remove oxygen present, as it has been stated by Elder and Rideal[28] that oxygen retards the reaction. Any condensable vapours were then removed by passing the gas through two traps cooled in solid CO_2-ether freezing

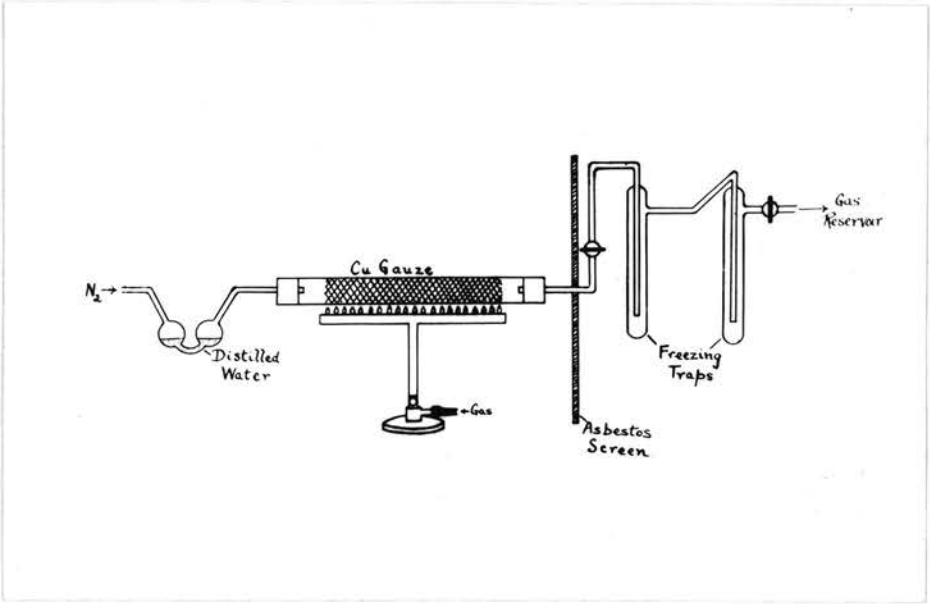


Figure VI.

mixtures. These traps were insulated, as far as possible, from the hot tube by an asbestos screen.

The first supply which was used was bubbled through concentrated sulphuric acid, instead of distilled water, and was passed through only one freezing trap. This supply, however, was found to have some undesirable effect on the vessel, as runs carried out after its use showed some anomalies - e.g. an abnormal decrease in pressure at the beginning of a run - which were not present previously. By replacing the sulphuric acid with distilled water, inserting two freezing traps instead of one, and passing the gas through slowly (1 to 2 bubbles per sec.) these anomalies disappeared. The amount of condensate in the second trap was very small, but observable, so it would thus appear that the two traps are required for the necessary removal of condensable vapours.

Phosphorus pentoxide was not employed for drying any of the gases for two reasons:

(a) Intensive drying was not necessary as some water was always introduced along with the peroxide vapour - the vapour being drawn from an aqueous solution.

(b) P_2O_5 was found to be a powerful catalyst to the reaction, and it was feared that some might be carried into the system along with the gas.

Oxygen./

Oxygen.

This gas was freed from any undesirable impurities by the train shown in figure VII. The procedure in this case consisted of bubbling the gas through distilled water, passing it through two gas wash-bottles containing alkaline potassium permanganate solution and dilute sulphuric acid respectively, and removing condensable vapours, as before, by means of two solid CO_2-ether freezing traps. The only impurity likely to be present after this treatment is nitrogen, and that only to a very small extent.

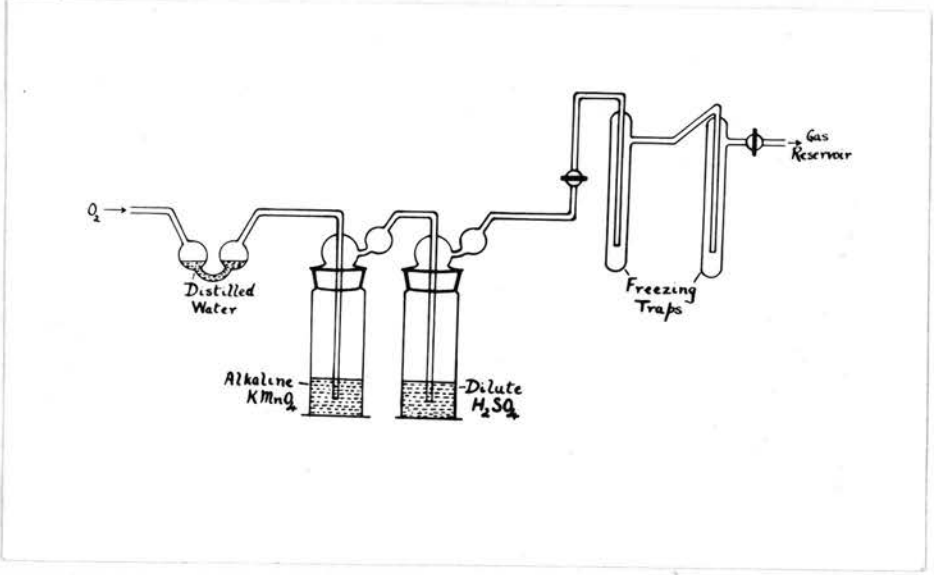


Figure VII.

Hydrogen.

The hydrogen employed was purified in the same way as the oxygen - i.e. it was passed through distilled water, alkaline permanganate, dilute sulphuric acid and two solid CO_2-ether freezing traps. After this treatment the only likely impurity is a small amount of oxygen, which was not considered important, as a little oxygen - from decomposition - is always present when the H_2O_2 is introduced, and, further, small amounts of oxygen had been shown to have a negligible effect on the reaction.

Carbon Dioxide.

According to Farkas and Melville[75] this gas, as supplied from a cylinder may contain as impurities, O_2, N_2, CO, H_2S and SO_2. The purification train employed therefore consisted of four gas wash-bottles containing respectively: alkaline potassium permanganate solution, sodium bicarbonate solution, copper sulphate solution and concentrated sulphuric acid, along with the two freezing traps. It was observed that the gas did not freeze out appreciably in the traps if it were kept flowing at a moderate rate. This train should remove any impurity which would be likely to have any undesirable effect.

Water/

Water Vapour.

As previously mentioned, the water vapour was drawn from a reservoir E (fig. V) which contained distilled water and was attached to the oil-pump line. Under the oil-pump vacuum this gave a pressure of about 12 mm. of water vapour at room temperature.

Experimental Procedure.

It has been shown by Maass and Hiebert[76] that the saturation vapour pressure over a solution of 99.98% hydrogen peroxide is 0.55 mm. at 4.65°C; 1.1 mm. at 15.2°C; and 1.5 mm. at 20.1°C. As the pressures of vapour used in the present investigation were of the order of 1 mm. (see page 31), it can be seen that these could be obtained from a 99% solution at room temperature. Furthermore, the composition of the vapour over peroxide solutions of various concentrations over the temperature range 30° - 60°C has been investigated by Giguère and Maass,[72] who showed that the percentage composition of the vapour over a solution of a certain strength at 30° was approximately the same as that over the same solution at 60°. They also showed that the percentage of hydrogen peroxide in the vapour over a solution was less than that in the solution. From their graph it appears that a 98% molar H_2O_2 solution (i.e./

(i.e. 99% by weight - see page 94) yields a vapour in which the concentration of peroxide is 91% molar. Thus, by taking a sample of the vapour over a 98% molar H_2O_2 solution at room temperature, one should obtain approximately 1 mm. pressure of a vapour which has a composition of 90 - 91% H_2O_2, 10 - 9% water, and a slight amount of oxygen, which is always present on account of decomposition. The criteria previously mentioned (pages 31-32) for a simple system would therefore be satisfied. This, in short, was the method employed in the present investigation.

To perform an experiment using the apparatus shown in figure V the procedure was as follows. The entire system was evacuated, first of all by the filter pump and then with the oil-pump. This precaution was necessary, for, if evacuation were carried out entirely by the oil-pump, the pumping speed was so rapid that there was danger of the pressure in the reaction vessel differing from the pressure in the gauge jacket (due to difference in path and capillary tubing) by an amount sufficient to fracture the gauge (normally about 5 mm.). The gauge and vessel only were then evacuated for a period of approximately 45 min., during which time the freezing mixture was removed from the reservoir C, thus allowing the peroxide to melt and come to room temperature. Taps T_3 and T_4 were then closed and tap T_1 opened/

opened, connecting the reservoir directly to the oil-pump. Tap T_5 to the sulphuric acid container D was always opened immediately the peroxide in C had melted. This served to remove water vapour formed by decomposition of some H_2O_2, and hence conserved the concentration of peroxide in the solution.

When the gases above the peroxide had been removed (some decomposition always occurred and an appreciable amount of gas was present after the solution had been standing at room temperature for a few minutes) the tap T_5 was closed. After about 30 sec. tap T_6 was also closed, the zero reading of the pointer taken, and tap T_3 opened. The movement of the pointer of the gauge was observed, and when the pressure in the vessel had reached the required value, taps T_3 and T_1 were closed, the reading of the position of the pointer on the eye-piece scale of the telescope T observed, and the time noted by a stop-watch. When this had been done the freezing mixture was replaced round reservoir C. Readings of the position of the gauge pointer were subsequently taken every five minutes up to thirty minutes from the introduction of the H_2O_2 and thereafter every ten minutes. These were the time intervals normally adhered to, but they were altered if conditions rendered it necessary. The "infinity" reading - corresponding/

corresponding to complete decomposition of the peroxide - was observed after leaving the H_2O_2 in the vessel overnight. On re-evacuation the zero reading for the gauge pointer was again checked to eliminate errors due to any accidental change in the telescope or gauge position between the first and final readings.

When a gas, such as oxygen or nitrogen, was introduced along with the H_2O_2 the method was slightly modified on account of the fragility of the gauge and the most satisfactory procedure was found to be as described below. The hydrogen peroxide was introduced into the reaction vessel and the initial readings of pressure and time observed as before. Tap T_6 was opened, the vapour present in the tubing removed by evacuation with the oil-pump for 1½ minutes, and tap T_6 again closed. Taps T_4, T_7 and T_8 were then opened and some gas introduced into this part of the apparatus so that there was a slight excess of pressure in the gauge jacket over the pressure in the vessel. This is necessary to prevent some of the vapour in the vessel escaping when tap T_3 was opened. Tap T_3 was opened and the gas entered the vessel equalising the pressures on the two sides of the gauge. At the same time more gas was slowly introduced into the system until the required pressure was established. All taps were then closed, the pressure/

pressure of gas read from the manometric system M_1, M_2, and the reading of the gauge pointer on the telescope scale noted. The time taken to perform the entire operation varied with the pressure of gas introduced, but was normally 4-7 mins. Thereafter, pressure changes in the reaction vessel were recorded as above.

This procedure was modified slightly in the case of water vapour, where the small pressures introduced were accurately read directly from the gauge and were balanced by introducing dry air into the gauge jacket through the tap T_2.

In view of the small pressures employed, and also the small volume of the capillary tubing, no correction was considered necessary for the vapour swept back into the vessel on introduction of gas.

Calibration of the Gauge.

Before performing any experiments the gauge had to be calibrated so that differences in scale readings on the telescope scale could be converted into pressure differences in mm. Hg. The method employed has already been described (page 50). As the gauge had to be as sensitive as possible to small pressure changes, a difference of pressure of 5-8 mm. (depending on the sensitivity) between the spring of the gauge and the jacket/

jacket was sufficient to cause fracture so great care had to be taken to prevent the pressure difference exceeding this value.

The method of calibration is shown by the following table in which is given a complete calibration for low (c. 1mm.), medium (c. 300 mm.), and high pressures (c. 600 mm.). It can be seen that the variation in sensitivity over the entire range is negligible.

Low Pressures.

Gauge Readings		Manometer Readings		Sensitivity
Initial Scale divisions	Final Scale divisions	Initial mm.	Final mm.	No. of scale divisions per mm.
89.6	8.9	759.8	754.0	13.9
94.7	6.0	758.9	752.6	14.1
91.9	6.9	758.5	752.5	14.15

Mean Sensitivity of Gauge at Low Pressures = 14.05 s.d./mm.

Medium Pressures.

94.3	5.9	427.9	421.6	14.0
94.1	7.0	428.0	421.8	14.0

Mean Sensitivity of Gauge at Medium Pressures=14.0 s.d./mm.

High Pressures.

s.d.	s.d.	mm.	mm.	No.of s.d./mm.
92.8	5.8	114.6	108.4	14.0
93.3	7.6	115.1	109.0	14.05
95.0	6.2	115.0	108.7	14.1

Mean Sensitivity of Gauge at High Pressures=14.05 s.d/mm

Smallest recordable pressure change = $\frac{1}{10}$ s.d. = 0.007 mm.Hg.

Other/

Other gauges employed had sensitivities of 54.1 s.d. per mm., 27.0 s.d. per mm. and 23.0 s.d. per mm. It was found possible to read the eyepiece scale of the telescope to 0.1 s.d. which gave the lowest observable change of pressure for the above gauges as 0.002 mm., 0.004 mm., 0.004 mm. respectively. The pressures were therefore calculated to the third decimal place in the case of the last three gauges, and to the nearest 0.005 mm. in the case of the first. In all cases a smooth curve was drawn through the points obtained by plotting pressure against time, and from this curve pressures could be determined fairly accurately to 0.001 mm. Hg.

Determination of Concentration.

As two molecules of the reactant decompose to give three molecules of product according to the equation:

$$2\,H_2O_2 = 2\,H_2O + O_2$$

the net result of decomposition at constant volume is an increase in pressure as the reaction proceeds. This increase in pressure will be equal to the amount of oxygen formed and half the amount of water formed. At complete decomposition the pressure in the reaction vessel, at constant volume, should - in the absence of any disturbing effects such as adsorption- have increased/

increased by an amount equal to one half the partial pressure of hydrogen peroxide originally present in the vapour. Thus, assuming that all the peroxide had decomposed when the "infinity" reading was taken (about 20 hours after the commencement of the reaction) and knowing the initial pressure of vapour introduced, the "molar percentage" of H_2O_2 in the original vapour should be given by the equation:

$$\left[H_2O_2\right]_m = \frac{2(p_\infty - p_o)}{p_o} \times 100 \quad \text{----------} \quad (1)$$

where p_o = initial pressure of vapour

p_∞ = pressure at complete decomposition.

In the presence of phosphorus pentoxide this equation becomes:

$$\left[H_2O_2\right]_m = \frac{2\,p_\infty}{p_o} \times 100$$

as p_∞ is the pressure of oxygen generated by complete decomposition of the peroxide, the water having been absorbed by the P_2O_5. It should be mentioned, however, that on account of an adsorption effect equation (1) had to be slightly altered as described later (see Discussion, page 104).

Furthermore, assuming that no oxygen is originally present in the vapour (this is not strictly accurate, as a slight amount of decomposition always occurs during introduction of the vapour), and knowing the original concentration of H_2O_2 in the vapour, the initial total pressure/

pressure and the pressure at any given time, the amounts of oxygen, water and hydrogen peroxide present in the vessel at that time can be determined by a simple calculation. The amounts of oxygen and water as calculated in this way are likely to diverge slightly from those actually present - the partial pressure of O_2 will be slightly higher than that calculated and the partial pressures of H_2O slightly lower, but the sum of the true partial pressures will be equal to the sum of the calculated pressures - while the concentration of peroxide will be correct. If the procedure described above (page 58) is carried out expeditiously, however, the amount of oxygen present in the original vapour should be very small and may be neglected (see Discussion page 107).

As an example of the method employed, a detailed example of the calculation of concentrations of water, oxygen and hydrogen peroxide is appended:-

Initial concentration of H_2O_2	=	84%
Initial pressure of vapour	=	0.741 mm.
Partial pressure of H_2O_2 in original vapour	=	$0.741 \times \frac{84}{100}$ mm.
	=	0.622 mm.
Partial pressure of H_2O in original vapour (assuming no decomposition had occurred)	=	0.741 - 0.622 mm.
	=	0.119 mm.
Total pressure at 10 min.	=	0.819 mm.
Increase in pressure	=	0.819 - 0.741 mm.
	=	0.078 mm.

Partial pressure of oxygen at 10 min. = 0·078 mm.

Pressure of water formed = 2 x 0.078 mm.

= 0.156 mm.

Partial pressure of H_2O at 10 min. = 0.119 + 0.156 mm.

= 0.275 mm.

Partial pressure of H_2O_2 at 10 min. = 0.622 - 0.156 mm.

= 0.466 mm.

Each run was analysed in this manner, and tables constructed showing the amounts of oxygen, water and hydrogen peroxide present in the vapour at convenient time intervals. Graphs showing the variation of total pressure, and partial pressure of hydrogen peroxide with time were also constructed.

In order to interpret the results of experiments with added gases, the method had to be slightly modified. In this case, as can be seen from the procedure described above (page 60) no measurement of the amount of decomposition occurring while the gas was being introduced, i.e. during the first five minutes or so, was possible. Also, the absolute pressures of vapour in the reaction vessel were not recorded by the gauge system after introduction of the added gas - the readings observed only gave increases of pressure due to decomposition of the peroxide. The interpretation of these results was therefore carried out in the following manner. The scale readings of the gauge pointer with respect/

respect to time were plotted on a graph, and the smooth curve drawn through these points was extrapolated to zero time. This point was taken as the pressure of vapour originally present and pressures corresponding to the other readings were then calculated on this basis. A slight uncertainty about the extrapolated portion of the graph is naturally inherent in this method, but by careful comparison with graphs obtained without the added gas this uncertainty can be cut down to a mimimum.

EXPERIMENTAL RESULTS.

I. PREPARATION OF HYDROGEN PEROXIDE.

In the following three tables are shown detailed analyses of the results obtained in each step of one complete concentration of a hydrogen peroxide solution. Table I refers to distillation of the crude solution, table II to distillation over silver sulphate, and table III to the final distillation. In table I the concentration of the liquid collecting in receiver C (figure II) was so small compared with that in receiver B, that estimation of all the fractions was not considered necessary.

Table I.

Concentration of H_2O_2 in the crude solution = 5.8%.

Fraction.	Concentration in Receiver B.	Concentration in Receiver C.
1	0.14%	0.03%
2	0.19%	
3	0.25%	
4	0.33%	
5	0.63%	0.30%
6	0.68%	
7	2.5 %	0.7 %
8	11.8 %	
9	68.3 %	

Table II.

Concentration of solution before distillation = 25% H_2O_2.

Fraction.	Concentration in Receiver B.	Concentration in Receiver C.
1	2.8%	0.4%
2	3.1%	0.3%
3	4.1%	
4	4.9%	0.4%
5	11.6%	1.3%
6	56.7%	2.6%
7	95.8%	Insufficient for analysis.

Table III.

Concentration of the solution before distillation = 70%

Fraction.	Wt. of H_2O_2 soln. analysed	Vol. of 0.1025N $KMnO_4$ reqd.	Concentration.
1	0.1361 gm.	29.20 ml.	37.5%
2	0.1123 gm.	59.00 ml.	91.8%
3 (a)	0.0508 gm.	28.80 ml.	99.0%
3 (b)	0.0596 gm.	33.89 ml.	99.1%

Volume of Fraction 3 = 1.5 ml.

II. DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR.

For convenience the experimental results are classified below; details of and conclusions from these results are appended under the heading "Discussion" (page 95). At the head of each table is given the relevant information regarding the conditions under which the experiments were carried out.

In all tables the following symbols are used:

$[H_2O_2]_m$ for initial "molar percentage" of H_2O_2 in the vapour;

$[H_2O_2]_i$ for initial partial pressure of H_2O_2 in the vapour;

$[H_2O_2]$ for partial pressure of H_2O_2 at any time;

$[H_2O]$ for partial pressure of H_2O at any time;

$[O_2]$ for partial pressure of O_2 at any time;

p_o for initial total pressure;

p'_o for corrected initial total pressure (see pages 99 -106);

p_∞ for final total pressure ("infinity" reading).

The suffix "(exp.)" denotes experimentally determined values, while "(calc.)" refers to calculated values.

Composition of the Vapour.

Table IV.

Large Reaction Vessel (Volume = 31.35 ml.).

Concentration of H_2O_2 in Solution = 78.4% molar.

Concentration in Vapour (according to Giguère and Maass[72]) = 39%

Normal Determination				P_2O_5 Determination		
p_o mm.	p'_o mm.	p_∞ mm.	$[H_2O_2]_m$ %	p_o mm.	p_∞ mm.	$[H_2O_2]_m$ %
1.18	1.15	1.37	38	0.93	0.20	43
0.97	0.94	1.23	37	0.90	0.16	36
0.96	0.91	1.07	35	0.75	0.15	40
0.92	0.89	1.06	38	0.61	0.12	39
		Mean	37%		Mean	39%

Difference between results by two methods = 39% - 37% = 2%

Effect of Oxygen.

Table V.

No Added Gas Present. Large Reaction Vessel.

Temperature of Reaction Vessel = 82.20°C.

Temperature of Gauge = 25.85°C. $[H_2O_2]_m$ = 80%

Experimental.		Values from Smoothed Curve.			
Time min.	Pressure mm.	Time min.	Pressure mm.	$[H_2O_2]$ mm.	$[H_2O]$ mm.
0	0.693	0	0.693	0.554	0.139
5	0.711	5	0.716	0.508	0.185
10	0.737	10	0.738	0.464	0.229
15	0.759	15	0.759	0.422	0.271
20	0.778	20	0.778	0.384	0.309
25	0.793	25	0.794	0.352	0.341
30	0.808	30	0.809	0.322	0.371
40	0.830	40	0.831	0.278	0.415
51	0.848	50	0.848	0.244	0.449
62	0.867	60	0.862	0.216	0.477

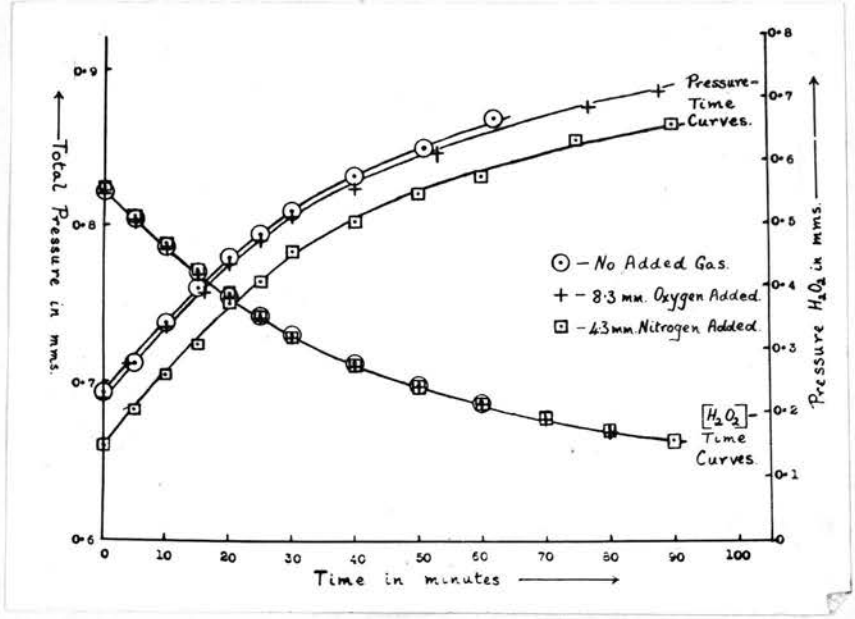

Total Pressure in mms.
Pressure H_2O_2 in mms.
Time in minutes
Pressure-Time Curves.
$[H_2O_2]$-Time Curves.
⊙ – No Added Gas.
+ – 8·3 mm. Oxygen Added.
⊡ – 4·3 mm. Nitrogen Added.
0·9
0·8
0·7
0·6
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
0
10
20
30
40
50
60
70
80
90
100

Table VI.

8.3 mm. Oxygen Added. Large Reaction Vessel.
Temperature of Reaction Vessel = 81.92°C.
Temperature of Gauge = 26.20°C. $[H_2O_2]_m$ = 80%.

Experimental.		Values from Smoothed Curve.			
Time min.	Pressure mm.	Time min.	Pressure mm.	$[H_2O_2]$ mm.	$[H_2O]$ mm.
0	0.689	0	0.689	0.550	0.139
4	0.711	5	0.712	0.504	0.185
10	0.734	10	0.734	0.460	0.229
16	0.756	15	0.755	0.418	0.271
20	0.774	20	0.774	0.380	0.309
25	0.789	25	0.790	0.348	0.341
30	0.804	30	0.805	0.318	0.371
40	0.822	40	0.827	0.274	0.415
53	0.845	50	0.843	0.242	0.447
77	0.874	60	0.857	0.214	0.475
88	0.882	70	0.869	0.190	0.499
		80	0.879	0.170	0.519

Table VII.

4.3 mm. Nitrogen Added. Large Reaction Vessel.
Temperature of Reaction Vessel = 82.20°C.
Temperature of Gauge = 25.50°C. $[H_2O_2]_m$ = 85%.

Experimental.		Values from Smoothed Curve.			
Time min.	Pressure mm.	Time min.	Pressure mm.	$[H_2O_2]$ mm.	$[H_2O]$ mm.
0	0.659	0	0.660	0.560	0.100
5	0.682	5	0.683	0.514	0.146
10	0.704	10	0.706	0.468	0.192
15	0.723	15	0.727	0.426	0.234
20	0.749	20	0.746	0.388	0.272
25	0.763	25	0.764	0.352	0.308
30	0.782	30	0.780	0.320	0.340
40	0.801	40	0.803	0.277	0.383
50	0.819	50	0.820	0.240	0.420
60	0.830	60	0.833	0.214	0.446
75	0.853	70	0.844	0.192	0.468
90	0.863	80	0.854	0.172	0.488
		90	0.862	0.156	0.504

Effect of Hydrogen Peroxide.

Table VIII.

Large Reaction Vessel. Temperature of Vessel = 80°C.

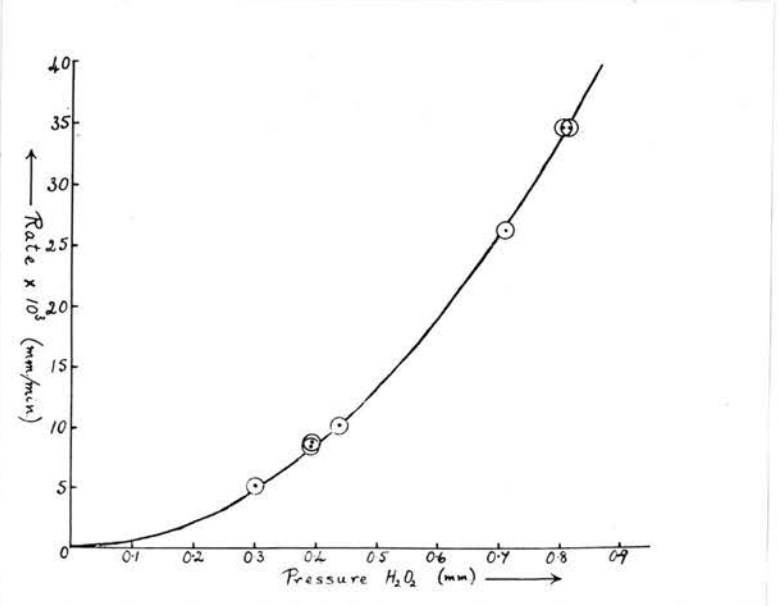
Temperature of Gauge = 25.5°C.

Partial Pressure of Water Vapour = 0.350 mm.

Po mm.	$[H_2O_2]$ m %	$[H_2O_2]$ mm.	Rate(exp.) mm./min.	$\frac{\text{Rate}}{[H_2O_2]}$	$\frac{\text{Rate}}{[H_2O_2]^2}$	Rate(calc.) mm./min.	$\frac{\text{Rate(exp.)}}{\text{Rate(calc.)}}$
1.150	82	0.800	0.0350	0.044	0.055	0.0352	0.995
1.140	70	0.790	0.0350	0.044	0.056	0.0343	1.02
1.050	68	0.700	0.0265	0.038	0.054	0.0270	0.98
0.785	84	0.435	0.0102	0.024	0.055	0.0102	1.00
0.741	84	0.391	0.0088	0.022	0.058	0.0084	1.05
0.740	80	0.390	0.0085	0.022	0.056	0.0084	1.01
0.650	77	0.300	0.0052	0.017	0.058	0.0050	1.04

Curve on graph and Rate(calc.) in above table calculated from the equation:

$$\text{Rate} = 0.055[H_2O_2]^2$$



Effect of Water Vapour.

Table IX.

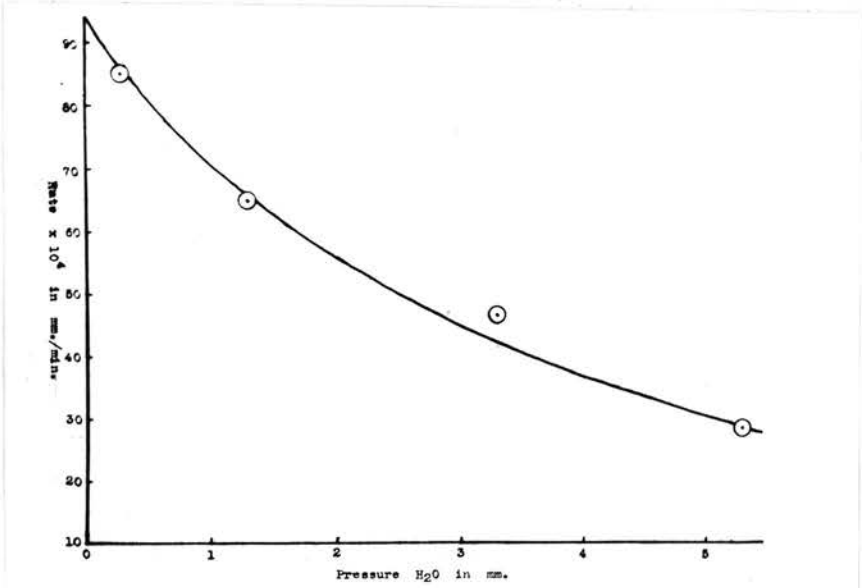
Large Reaction Vessel. Temperature of Gauge = 26.30°C.

Partial Pressure of H_2O_2 = 0.400 mm.

Temperature of Vessel °C.	$[H_2O]$ mm.	Rate(exp.) mm./min.	Rate(calc.) mm./min.	Rate(exp.) / Rate(calc.)
82.10	0.284	0.0085	0.0086	0.99
82.20	1.281	0.0065	0.0066	0.985
82.20	3.289	0.0047	0.0042	1.12
81.70	5.289	0.0029	0.0029	1.00

Curve on graph and Rate(calc.) in above table calculated from the equation:

$$\text{Rate} = \frac{0.0094}{(1 + 0.15[H_2O])^2}$$

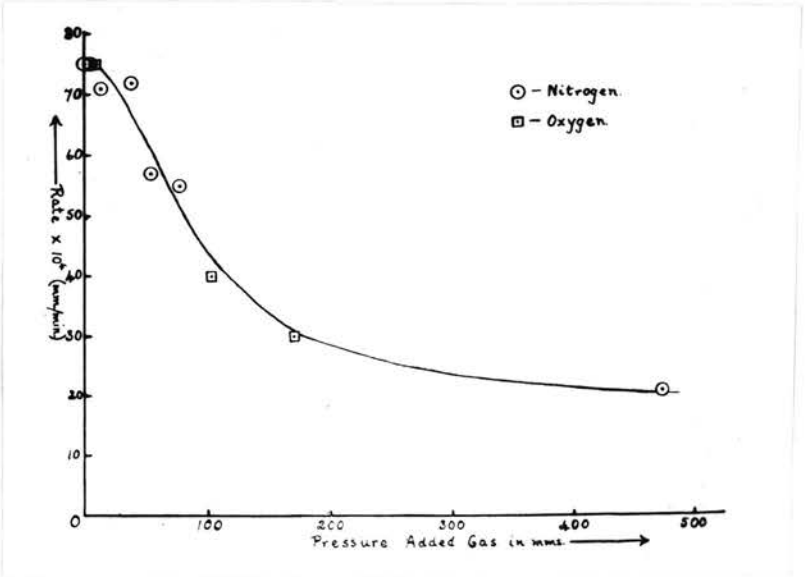


Effect of Added Gases.

Table X.

Large Reaction Vessel. Temperature of Vessel = 82.2°C.
Temperature of Gauge = 26.20°C. $[H_2O] \fallingdotseq 0.27$ mm.

$[N_2]$ mm.	$[O_2]$ mm.	$[H_2]$ mm.	$[CO_2]$ mm.	$[H_2O_2]_i$ mm.	$[H_2O_2]$ mm.	Rate mm./min.
-	-	-	-	0.554	0.400	0.0075
4.3	-	-	-	0.560	0.400	0.0075
13.5	-	-	-	0.535	0.400	0.0071
37.8	-	-	-	0.558	0.400	0.0072
52.9	-	-	-	0.580	0.400	0.0057
76.3	-	-	-	0.540	0.400	0.0055
471.6	-	-	-	0.563	0.400	0.0021
-	8.3	-	-	0.550	0.400	0.0075
-	102.2	-	-	0.542	0.400	0.0040
-	169.2	-	-	0.540	0.400	0.0030
-	499.4	-	-	(0.520)	(0.400)	(0.0030)
-	-	-	-	0.856	0.600	0.0245
-	-	2	-	0.812	0.600	0.0220
-	-	10	-	0.824	0.600	0.0205
-	-	-	11.4	0.826	0.600	0.0222



DISCUSSION.

I. PREPARATION OF HYDROGEN PEROXIDE.

Although an adaptation of the method of Kilpatrick, Reiff and Rice[3] has been used for the preparation of the concentrated solution of hydrogen peroxide employed in the present investigation, it may be observed that the ultimate aim has been entirely different in each case. The original method was devised as a means of obtaining a high yield of a fairly concentrated chemically pure solution of hydrogen peroxide in water, and no emphasis appears to have been laid on the time taken to effect this result, while in the present case the purpose has been to prepare a very concentrated chemically pure aqueous solution of hydrogen peroxide in a convenient manner which was neither excessively time-consuming nor too laborious, and no special emphasis was laid upon yields, although, in the interests of economy, it is of course necessary that the yields should be as high as practicable.

On commencing this work therefore, it was thought that, of the two methods then available, the most promising was that of Kilpatrick, Reiff and Rice - the other was that of Maass and Hatcher[2] (page 10), details of the method of Fehér[4] (page 11) not being then known. The reasons for this preference were that

(a)/

(a) no special intricate pieces of apparatus, such as the sulphuric acid evacuating pump employed by Maass and Hatcher, were necessary,

(b) the 'double distillation' effect (vide infra) should render the process reasonably rapid,

(c) several preliminary experiments testing out this method had been performed in this laboratory by E. Paterson, who showed that the method was capable of development to give greater concentrations than those reported by the original investigators.

The preparation of the crude solution (page 35) was carried out in the manner detailed in the original paper.[3] The main point to be noted in connection with this is the need for careful control of temperature; if the temperature exceeded 10°C during any part of the process considerable decomposition occurred. If reasonable precautions were taken this part of the procedure proceeded smoothly without an undue amount of decomposition.

With regard to the distillation, the original method is rather ingenious and has, in the main, been adopted here. Instead of the normal single receiver, two were employed in series, the second being cooled to a lower temperature than the first. This had the advantage that a "double distillation" was effected in the one apparatus, i.e. during the normal distillation some/

some of the solution in the first receiver was distilled over into the second, thus concentrating the solution in the first.

The amount of liquid collecting in the second receiver depends on two factors - (a) the amount of condensate resulting from the second part of the distillation, which should be small as this occurs at a low temperature (0°C); (b) the proportion of the vapour which escapes the first trap but is condensed in the second and which should also be small, but will largely depend on the rate of distillation. Under normal conditions therefore both these factors should be small and it would be expected that the volume of liquid collecting in the first receiver would be considerably greater than that in the second. This was actually found in practice (page 43).

In addition it was always found that the liquid in the second receiver was much more dilute than that collecting in the first. Here again the factors which determine the volume in the second receiver are involved. The first of these would cause the solution to be much more dilute, because the vapour pressure of water at 0°C is much greater than the vapour pressure of hydrogen peroxide[76] while it would be expected that any condensate due to the second would have approximately the same concentration in both receivers. As the resultant/

resultant concentration was considerably less, it can therefore be deduced that little vapour escapes condensation in the first receiver and that most of the liquid in the second receiver is due to distillation over of the liquid in the first.

The entire distillation is, indeed, based on the difference between the saturation vapour pressures of water and hydrogen peroxide - e.g. saturation vapour pressure of water at 50°C is 92.5 mm., while that of H_2O_2 is only 11 mm. The net result if no complex with a lower vapour pressure is formed is, therefore, that the water vapour tends to come over first accompanied with very little hydrogen peroxide while the solution being distilled becomes more and more concentrated in H_2O_2 so that the last few millilitres will be almost pure H_2O_2. This considerable difference in vapour pressures also explains why the temperature has to be raised towards the end of the process to keep the distillation going at a reasonable rate.

In view of the fact that the most concentrated hydrogen peroxide should, according to theory, distil over in the last few millilitres, instead of collecting the distillate in only one fraction in each receiver according to the original method, it was decided to collect the distillate in a number of small fractions. If the above reasoning is correct, it would be expected that/

that the first few fractions collecting in both receivers would be very dilute, while the last few fractions collecting in the first receiver would be very concentrated. Hence, by rejecting the dilute fractions and employing only the more concentrated fractions for further concentration and purification, considerable time would be saved over the whole process. That this postulate was correct can be very clearly seen from tables I and II. The concentrations effected by distillation of the crude solution in this manner (table I) are especially noteworthy, as the last fraction collecting in receiver B, from distillation of a solution whose initial percentage of peroxide was only 5.8%, had a concentration of 68% H_2O_2. The concentration of the last fraction naturally depends on the amount of liquid collected in that fraction, and in the above experiments it was usually adjusted that this volume was 4-5 ml. for a crude solution obtained from 100 ml. 20% sulphuric acid. To effect this the receivers were changed for the last time when well defined striae were observed in receiver B owing to mixture of a concentrated distillate with a weaker one.

Owing to rejection of so much of the weak peroxide solution, and the decomposition which inevitably occurs during addition of the sodium peroxide to the sulphuric acid and distillation, it cannot be expected that the yields/

yields obtained by the above process will be very high. However, if the last two fractions obtained from the first distillation were mixed in suitable proportions, about 11-12 ml. of a 30% H_2O_2 solution could normally be obtained, which is equivalent to a yield of 50% of the theoretical.

It had been observed by Maass and Hatcher[2] that, if the vacuum distillation was carried out in the usual way using an oil-pump, the oil tended to thicken owing to oxidation, and for their method they devised a special sulphuric acid vacuum pump, which, as well as evacuating the system, also provided a certain amount of concentration, the sulphuric acid acting as a desiccating agent. It was later shown by Kilpatrick, Reiff and Rice,[3] however, that it was not necessary to construct a special pump, as no thickening of the pump oil was observed when a sulphuric acid trap was inserted between the distillation apparatus and the oil-pump. This trap has a twofold effect - it both prevents thickening of the oil of the pump, and acts as a desiccator, thus concentrating the vapour. The reason for the first of these is not quite clear, unless it absorbs some hydrogen peroxide which would otherwise pass through and oxidise the pump oil. In the present work the observation of Kilpatrick, Reiff & Rice has been confirmed, for in the presence of this sulphuric acid trap/

trap no deleterious effect on the oil or mechanism of the pump has been observed.

In all distillations it was found that higher concentrations were obtainable by performing the process at a reasonable rate rather than by allowing it to proceed slowly. This may be considered peculiar as it would be expected that at the higher temperature a greater amount of decomposition would occur in the liquid in the distilling flask. This did, of course, occur, and the total yields were probably not as high as those which would be obtained at the lower temperature, but the fact remains. Two possible explanations suggest themselves, and the total effect is probably due, to a certain extent, to both.

(a) If the distillation was carried out rapidly, a smaller amount of the distillate condenses on the walls of the condenser, most condensation occurring in the receiver which is cooled in ice water. The amount of decomposition occurring in the latter is much less than on the condenser walls, which are at a higher temperature.

(b) With rapid distillation a smaller amount of peroxide vapour comes in contact with the condenser walls, on passing through the condenser, and it would be expected that the amount of decomposition would be smaller than with slow distillation, where more would be expected/

expected to touch the walls. A certain amount of decomposition is inevitable from decomposition of the condensate collecting in the condenser as it flows down into the receiver. It would appear, therefore, that to obtain a peroxide solution of high concentration, the distillation should be carried out as expeditiously as possible, as the "time" factor seems to have more influence on the ultimate result than does temperature of distillation.

The last fraction distilling over, i.e. the most concentrated fraction, always had a rather viscous appearance, and had a tendency to collect in droplets on the condenser wall, with consequent decomposition. To eliminate, as far as possible, loss due to this cause a vertical condenser was employed, but even here, the droplets became quite an appreciable size before they flowed down into the receiver. As mentioned above, well-defined striae were observed when the concentrated condensate came in contact with a weaker one, which would also seem to indicate a viscous tendency, or at least, a considerable difference in density. The most concentrated liquid, however, was clear and mobile and did not appear to be much more viscous than water, which is in accordance with the measurements of Maass & Hatcher[2], who found the two viscosities to be very close in magnitude.

Another/

Another peculiarity which was observed was that even the most concentrated solution appeared to be quite stable in the receiver in which it was collected, even if that receiver were shaken. If it were poured into another vessel, however, decomposition immediately commenced, as was visible from the bubbles of gas appearing in the solution. These bubbles all appeared to originate on the wall of the vessel. For the estimation, samples were taken from the liquid by means of a small pipette. Some of the liquid was sucked up the pipette, allowed to flow out and then some more sucked up. The actual sample analysed was taken from this second quantity, and it was found with this procedure that little or no decomposition was visible in the pipette. The relative stability of concentrated solutions was also observed, especially under vacuum. If a vessel containing the very concentrated solution (99% H_2O_2) was evacuated by the oil-pump at room temperature, very little decomposition was observed, but, when the solution had become less concentrated, bubbles of gas appeared very readily on evacuation. This, along with another effect described below, was used as a rough guide to the strength of the peroxide used in the subsequent experiments, for when the percentage fell below approximately 95%, gas bubbles were much more readily evolved than when the concentration was about/

about 99%. These observations corroborate in a qualitative manner many of the effects previously discovered and mentioned in the Introduction, i.e. the relative stability of concentrated solutions, the fact that these solutions apparently have the effect of destroying active centres for decomposition (page 25) (indicated by stability in the original receiver and in washed-out pipette), and the heterogeneity of the reaction (decomposition appeared to occur mainly at the surface of the vessel).

The last effect was also shown in another way. It was observed that when peroxide, which had been frozen at - 80°C, was being allowed to melt, and when there was some solid in contact with the solution, bubbles of gas were given off slowly at the solid-liquid interface, which raises the interesting point that solid H_2O_2 apparently acts as a catalyst for decomposition of its own liquid. This apparent paradox is probably due to the fact that the solid provides a surface at which decomposition occurs.

Maass and Herzberg[77] have made the observation that solutions of peroxide are very easily supercooled. This has also been corroborated. When the concentration of peroxide in the solution was about 99%, no difficulty was encountered in getting the liquid to freeze on immersing the vessel containing it in a solid CO_2-ether solution (about - 80°C). When, however, the solution became/

became weaker (below about 95%), the vessel with the peroxide solution could be immersed in the freezing mixture for an indefinite period without crystallisation occurring, unless the vessel were tapped or disturbed in any way when crystallisation immediately occurred. If the concentration was below 90%, it was difficult to crystallise the peroxide even by tapping the vessel. This was used as another rough guide to the strength of the peroxide in the reservoir.

It has been reported that very concentrated peroxide solutions are liable to explode very readily.[78] However, no explosive tendency was observed during any part of the present work, under the conditions detailed above.

Finally, it may be stated that the method of preparation evolved above is very convenient for use when small quantities of chemically pure very concentrated aqueous solutions of peroxide are required for quantitative work.

II. DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR.

Experimental Discussion.

Before discussing the experimental results, there are several points with regard to the experimental part of the work which are worthy of consideration.

The apparatus described above is essentially the system employed extensively by Ritchie and co-workers[79] for investigations of, inter alia, the hydrogen-chlorine reaction, the hydrogen-bromine reaction and the decomposition of ozone. It has the advantage that pressure changes are measured by an all-glass system, and thus any effect which might be imposed on the reaction by the use of a mercury or oil manometric system is eliminated. In the present case it again proved very satisfactory.

In the above mentioned systems it was found that particular attention had to be paid to the selection of a suitable tap-grease, as these were found to have considerable effects on the reaction. The most suitable was found to be Apiezon grease L, which had the minimum effect, and as is apparent from the description of the apparatus, it was used with one exception, throughout the present work. This exception was in the case of the apparatus shown in figure III where the ground joint K became hot towards the end of the distillation/

distillation with the result that the grease became fluid and tended to be sucked into the apparatus, thus causing a leak and, possibly, some decomposition of the hot vapour. In this case Picein wax was employed and found to be satisfactory. The first set of experiments described below (page 95) were designed to test the effect of tap-grease on the cool vapour (vapour from the solution at room temperature), but on account of other complicating factors the actual effect of the tap-grease was obscured. It was evident, however, that the effect, if any, was normally very slight.

On the hot vapour (i.e. about 80°C) the tap grease did appear to have some effect, for, if a distillation was carried out in an apparatus where the hot vapour had to pass through a greased tap (as was the case in the first modification of the apparatus shown in figure IV) the resulting concentration was less, by about 10%, than the concentration obtained in the absence of the tap.

All experiments, except those performed to investigate the effect of temperature, were performed with the reaction vessel at a temperature of about 80°C, because it was expected that, at this temperature, the rate would be reasonably rapid,[27] and also results obtained at this temperature would be comparable with those of previous workers, who employed temperatures in the region/

region 76 - 98°C.[27,28,29] When working at this temperature difficulty was originally experienced in getting sufficiently accurate temperature control with the thermostatic system employed.

It is desirable that the changes in pressure due to temperature changes should be below the minimum pressure changes readable on the gauge. This requirement is not exacting so long as the pressure in the vessel is of the order of 1 mm., as is normally the case, but when the pressure is greater owing, for example, to added gas it becomes much more exacting. The most sensitive system used was accurate only to ± 0.15°C; the control in this case being an electrically operated mercury expansion control, heat being supplied by a black-coated carbon filament bulb (to prevent any possible photochemical effect) immersed in the bath, in conjunction with a gas burner below the bath, this burner being so adjusted that it gave sufficient heat to maintain the bath at a temperature of approximately 5° below the desired temperature. The water in the bath was kept in constant motion by an electrically driven stirrer, and the bath was well lagged with asbestos to prevent heat losses. With this system no correction for temperature was required with pressures up to 20-30 mm. ~~pressure~~. Above this, corrections had to be applied for temperature, and these were found experimentally by admitting some inert gas into the vessel/

vessel and recording pressure changes for certain changes in temperature, because, owing to various time-lags in the system, the actual pressure change for any recorded temperature change was not quite that calculated from Boyle's and Charles' Laws. The same method was employed to find the effect due to small temperature changes in the gauge jacket. The following table gives one such determination:-

Pressure of gas (nitrogen) = 100.3 mm.

Temperatures.		Temperature Changes.		Gauge Reading (R)	ΔR	Change in Pressure (Δp) (mm./0.1°C)	
Thermostat °C	Gauge °C	Thermostat °C	Gauge °C	s.d.	s.d.	Thermostat	Gauge
82.05	25.82			63.4			
		0.15	0.00		0.6	0.017	-
82.20	25.82			64.0			
		0.50	0.00		2.0	0.017	-
81.70	25.82			62.0			
		0.90	0.10		3.3	(0.017)	0.013
82.60	25.92			65.3			
					Mean	0.017	0.013

($\Delta p/0.1^{\circ}C$ for 100 mm. (calculated) = 0.028 mm.)

In the above determination the thermostat and gauge were slightly overheated to give easily measurable temperature and pressure changes. The same procedure was carried out for 500 mm. pressure, and here the corrections were:-

$\Delta p/0.1^{\circ}C$ for Thermostat = $\Delta p/0.1^{\circ}C$ for Gauge = 0.074 mm.

(Calculated Value = 0.141 mm.)

These/

These experimentally determined corrections were applied to all runs where the pressure changes due to temperature variations were measurable on the gauge system. It had to be assumed that the various time-lags in the system remained constant; in any case, the corrections were not large, and gave, normally, a satisfactorily smooth decomposition curve.

In order to prevent the heat from the bath heating the tap-grease lubricating the joint J and the tap T_3 (figure V), and possibly causing excessive decomposition of the H_2O_2 vapour at these points (page 88), the thermostat was provided with a metal cover well lagged with asbestos. When the electric heater was employed in place of the thermostat, the joint J was kept cool by means of a jet of compressed air, and tap T_3 was sufficiently far away to be unaffected by the heat from the furnace.

So that the main decomposition might occur in the silica vessel, the volume of the capillary tubing between the vessel, tap T_3 and the gauge was kept as small as possible - the total volume of the tubing was about 3% of the vessel volume. That the main decomposition occurred in the vessel was shown in preliminary experiments where the capillary was closed by a sealed off ground joint. The rate of decomposition in the capillary alone was 2-3 times that observed in a run with/

with the vessel in position, but, as the volume of the vessel was so large compared with that of the capillary, calculation shows that, in practice, the observed rate was almost entirely due to decomposition in the vessel.

In the first few runs with the apparatus, carried out as described above (pp. 58-60), a peculiar effect was observed, i.e. no increase in pressure was observable even after several hours. After several attempts, however, increases in pressure became apparent and, after several more, became fairly reproducible. This effect was only observed in the case of the large silica vessel (volume = 31.35 ml.), and not in the case of the other, although the first few results obtained with the latter were rather erratic. That this was not due to tap-grease was shown by the fact that no such effect was observed after tap T_3 or the joint J were regreased. The irregularity of the initial results is therefore apparently due to a necessity for "ageing" the silica vessel, a requirement which has been noticed by previous workers.[80]

Reproducibility of results was, on the whole, reasonable, but, in certain cases, appreciable differences were observed in experiments carried out apparently under the same conditions. These irregularities could usually be traced to variation in the concentration of hydrogen peroxide in the vapour introduced into the vessel/

vessel, and could be allowed for by employing, in any calculations, the percentage obtained from the "infinity" readings. Another possible cause of variation was change in the surface of the vessel.[29] Variations in concentration of H_2O_2 in the vapour depended on several points inherent in the method employed, e.g., if the liquid in the reservoir was not sufficiently warm, it took longer to establish the required pressure in the vessel, with consequent greater chance of decomposition in the tubing between the reservoir and the vessel; if the liquid became too warm some decomposition occurred in the liquid during introduction of the vapour with the consequence that some of the decomposition products entered along with the vapour, lowering the concentration.

It should be mentioned that it was not always possible to leave the vapour in the vessel overnight to obtain the "infinity" reading. In those cases, an approximate "infinity" reading was obtained, by extrapolation, from the time-pressure curve, and comparison of this curve with others where the "infinity" reading was known. It was possible in this way to obtain concentrations to within 5%. Several difficulties were encountered in the calculation of concentrations for "infinity" readings, and these are discussed below.

It is noteworthy that the percentage of H_2O_2 obtained/

obtained from the vapour, as measured by pressure changes, is the molar fraction of H_2O_2 expressed as a percentage (this follows from the equation on page 64) and thus it is convenient to work in these units. The relationship between this "molar percentage" and the weight percentage is expressed in the equation:

$$\left[H_2O_2\right]_m = \frac{x/34}{x/34 + (100 - x)/18} \times 100$$

where $\left[H_2O_2\right]_m$ is the molar percentage; $\underline{x}$ the percentage by weight; $\underline{(100 - x)}$ the percentage water by weight; $\underline{18}$ and $\underline{34}$ the molecular weights of water and hydrogen peroxide respectively. Simplification of this equation gives:

$$\left[H_2O_2\right]_m = \frac{1800\ x}{3400 - 16\ x}$$

Thus, a solution containing 99% H_2O_2 by weight has a concentration of 98.1% molar.

During the course of the experiments it was observed, as would be expected, that the concentration of H_2O_2 in the reservoir tended to decrease with time. This concentration was examined by determining, from the "infinity" reading, the concentration of peroxide in the vapour delivered into the vessel from the solution, and by employing the data of Giguère and Maass[72] to give the concentration in the solution. That this procedure is justified is shown by the results of the following section/

section.

It was found, for example, at one time, that the concentration in the vapour was 84%, while three weeks later it was 78%. These figures relate to solution concentrations of 96% and 94% respectively. As the difference between these figures gives the amount of decomposition occurring in the solution over three weeks while runs were being performed daily - i.e. the solution was melted and re-frozen every day - it is evident that preservation of the solution, by freezing in a solid CO_2-ether mixture and connecting it to a sulphuric acid desiccator when in the liquid state, was very effective.

When the concentration in the vapour was considered too low, the solution was re-concentrated by immersing the reservoir, under vacuum, in hot water (at about 60°C) boiling some off, and using the residue as the stock solution. One such concentration gave a figure of 100% for the concentration of H_2O_2, as determined by the permanganate titration.

Discussion of Results.

After a few preliminary runs to stabilise the system, the first point investigated was the composition of the vapour delivered into the vessel from a solution of/

of known strength. The composition of vapours over solutions of various concentrations has already been investigated by Giguère and Maass,[72] and by comparison of their results with the present results it was hoped to get an estimate of the amount, if any, of decomposition occurring while the vapour was being introduced into the reaction vessel, and from this to estimate whether the tap-grease had any considerable effect on the cold vapour.

The solution, from which the vapour was drawn, was one which was used for several preliminary experiments to test out the apparatus, the concentration of H_2O_2 in the liquid being 78.4% molar (87.3% by weight). The vapour above such a solution, according to the data of Giguère and Maass, should have a concentration of H_2O_2 of 39% molar. The assumption is here made that the vapour over a solution at room temperature has the same composition as that over a solution in the temperature range 30-60°C, over which range it has been shown to be constant.[72]

In order to test this figure under the experimental conditions employed, determinations of concentrations in the vapour were performed in two different ways:

(a) In the normal decomposition manner (pages 58-60) the results from which should obey the theoretical equation (page 64):

$$\left[H_2O_2\right]_m = \frac{2\,(p_\infty - p_o)}{p_o} \times 100$$

(b) In the presence of phosphorus pentoxide which absorbs all the water present and, hence, gives the equation:

$$\left[H_2O_2\right]_m = \frac{2\,p_\infty}{p_o} \times 100$$

These two methods give results relating to different conditions; the first takes no account of any decomposition products present in the vapour when it is introduced into the vessel, while the latter gives a measure of the total amount of oxygen present in the vapour and, hence, the composition of the vapour as it was drawn from the solution. The latter should, therefore, yield results comparable with those of Giguère and Maass, while the concentrations obtained from the former should give a measure of the concentration of peroxide in the vessel at the commencement of the reaction, and, by comparison of the two, a measure of the amount of decomposition occurring while the vapour was being introduced should be obtained.

The percentages obtained by the two methods are shown in table IV (page 71). It is evident that the difference between concentrations derived from the two methods is slight (2%) and it would seem that very little decomposition occurs during introduction of the vapour to the vessel. However, although the concentrations obtained from method (a) are, on the whole, only slightly/

slightly lower than those from method (b), the interpretation is not so simple as it appears, on account of several points which are discussed below.

The first very obvious effect, which, however, had no influence on the actual concentrations obtained, was the fact that phosphorus pentoxide acted as a powerful catalyst to the reaction. In the presence of P_2O_5 the reaction was normally complete in less than five minutes, while in its absence, it was doubtful if the reaction were complete even in 22 hours. There are probably three main reasons for this - (a) provision of a large amount of surface by the finely divided P_2O_5 powder; (b) a possible slight effect due to the removal of water (see pages 113-114); (c) a heating effect due to combination of water with the P_2O_5. From later results it would seem that (a) and (c) together have almost certainly the greater influence.

A few of the P_2O_5 results gave concentrations higher than those expected from the data of Giguère and Maass. This is apparently due to decomposition in the solution while the peroxide vapour was being introduced. Small bubbles were always observed in the liquid - sometimes only a few, but sometimes quite a number - and the oxygen from this source was mixed with the vapour introduced into the vessel. The effect on the calculated percentage would therefore be towards higher/

higher values in the P_2O_5 experiments and towards lower values in the normal experiments. As indicated above this effect was somewhat variable and may be one of the main factors causing lack of reproducibility.

An observation made in all determinations with this apparatus had considerable effect on the interpretation of the present and all subsequent results and may profitably be discussed here. Certain points mentioned anticipate results which will be discussed later, but for full interpretation of the above results it appears necessary to discuss the effect rather fully.

A very slight pressure decrease was always observed at the beginning of a run, which decrease was greater the lower the pressure of hydrogen peroxide in the vapour. This decrease in pressure was ascribed mainly to adsorption of water vapour on the walls for several reasons - (a) it could not be due entirely to H_2O_2 as it was more pronounced the less the amount of peroxide present; (b) it was much too pronounced to be due to the small amount of oxygen present; (c) the same effect was observed in an enhanced form on introducing water vapour alone into the vessel. That adsorption of hydrogen peroxide is also involved to some extent was apparent from later results when figures of over 100% were obtained for concentrations in the vapour at low pressures (0.2 - 0.3 mm.). In the latter case/

case the total pressure of water vapour in the vapour is small, and here H_2O_2 appears to be appreciably adsorbed. From consideration of all these facts, however, it would appear that adsorption of water vapour is relatively the greater.

It was also observed that when concentrated H_2O_2 solutions were employed - e.g. the 98% molar solution - this pressure decrease was complete in about 1 second after the tap to the reaction vessel was closed, while with a more "dilute" vapour - e.g. the 39% H_2O_2 vapour from the 78.4% solution - the original rapid decrease, which was much greater in this case, was frequently followed by a slow pressure decrease, or no pressure change, for a few minutes before the pressure began to increase, as it should normally do. This would indicate that the adsorption is only complete after a few minutes, but in the case of the concentrated solution the initial reaction rate is sufficiently rapid to mask the effect, while in the case of the weaker solution this is not so. In either case the initial rates will, of course, be lower than the true rates.

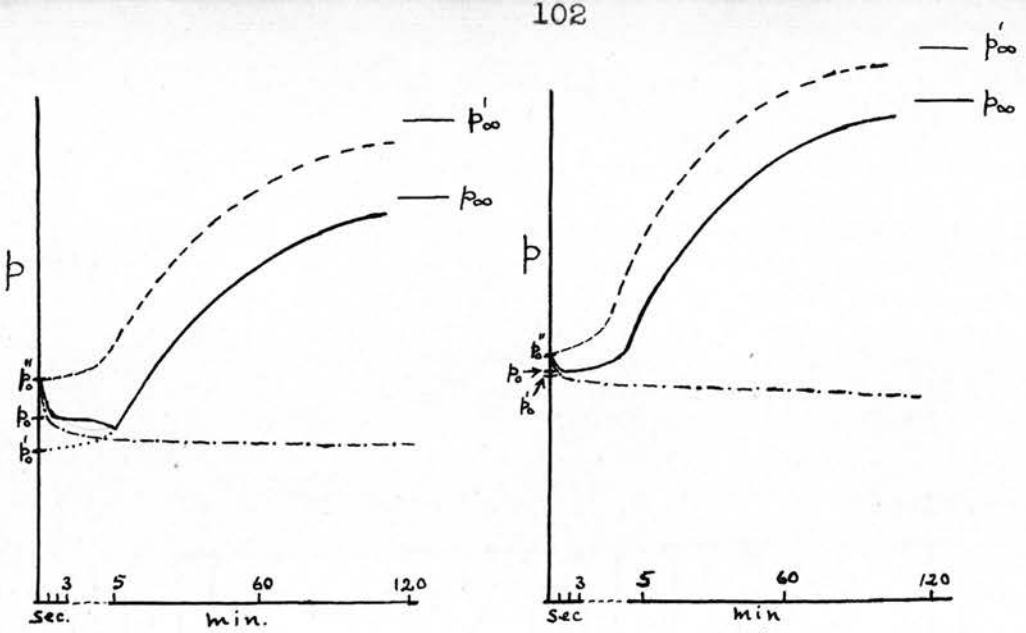
It would be expected, however, that there would be one exception to this - that is in the case where the decomposition of H_2O_2 initially adsorbed on the wall and not measured by the system exactly balances the decrease in pressure due to adsorption. In this case/

case the true decomposition curve and the experimental curve should coincide - or more accurately, the true decomposition curve will be parallel to the experimental curve, the "pressure distance" between the two being given by the amount of the original rapid adsorption. This has actually been observed and will be discussed later (page 122).

Confirmation of the fact that adsorption occurred over several minutes even in the case of concentrated solutions was supplied later by some experiments carried out with the apparatus evacuated to a residual pressure of 0.00025 mm. by means of a mercury vapour pump. The apparatus was evacuated in this way for four hours, so that there would be greater chance of removal of any adsorbed film. In this case, the slow pressure decrease was observable for about 5 minutes, but after that time the decomposition curve followed its normal course.

The observed pressure-time curve would then appear to be formed by the summation of three curves: (1) the true decomposition curve - i.e. relating to the amount of hydrogen peroxide measured by the system - which gives an increase in pressure; (2) decomposition of H_2O_2 initially absorbed but not measured by the system, also giving an increase in pressure; (3) the adsorption curve which gives a decrease. The effect of the second

of/



---------- True Decomposition Curve.

———————— Experimental Curve.

..... Extrapolated Part of Curve.

-.-.-.-.-.-.- Adsorption Curve.

p_0 and p_∞ Experimental Initial and Final Pressures.

p''_0 and p'_∞ True Initial and Final Pressures.

p'_0 Initial Pressure from Extrapolated Curve.

Figure VIII.

of these is discussed later, so we may neglect it for the moment. A sketch of the curves that might be expected for the other two is given in figure VIII where the first portions of the curves are considerably magnified to show clearly the initial adsorption.

At the low pressures employed and in view of the small amount of water originally present, it seems improbable that the amount of water adsorbed would not increase with increase of the partial pressure of water vapour/

vapour in the vessel - an effect which would be more pronounced in the case of the concentrated peroxide curve than in that of the other. The influence of this on the rates of reaction will be discussed later as here we are only concerned with the effect on the apparent concentration.

The magnitude of the quick adsorption at the commencement of the reaction is doubtful as it was too rapid to be readable on the gauge. It was roughly estimated, however, that in the case of the 98% molar solution it was of the order of 0.01 mm., or less, while for the dilute solution (78.4%) it was of the order of 0.1 mm.

Considering the effect of adsorption on the calculated concentration of H_2O_2, it is evident from figure VIII that if the expression

$$\left[H_2O_2\right]_m = \frac{2(p_\infty - p_o)}{p_o} \times 100 \quad \text{--------} \quad (1)$$

were used as it stands the values obtained would be somewhat in error. The correct value for the concentration would be given by:

$$\left[H_2O_2\right]_m = \frac{2(p'_\infty - p''_o)}{p''_o} \times 100 \quad \text{-------} \quad (2)$$

where p'_∞ is the total pressure on complete decomposition in the absence of adsorption and p''_o is the initial pressure in the absence of adsorption.

If/

If the pressure-time curve is extrapolated to zero time, however, the experimental equation becomes:

$$\left[\underline{H_2O_2}\right]_m = \frac{2\,(p_\infty - p_o')}{p_o'} \times 100 \quad \text{------} \quad (3)$$

where $\underline{p_o'}$ is the pressure at zero time for the extrapolated curve, Equation (3) should give a much more accurate value than (1) for the concentration of peroxide in the vapour - at least for vapours from dilute solutions - both because $(p_\infty - p_o')$ is much nearer $(p_\infty' - p_o'')$ than is $(p_\infty - p_o)$, and also p_o' is less than p_o and hence tends to raise the concentration slightly. Further, any initial adsorption of peroxide not measured by the system would also tend to increase the percentage. From comparison of the curves for "dilute" and "concentrated" vapours it is also evident that discrepancies between the true and observed values will be greater in the case of vapours derived from concentrated solutions - i.e. in the curve for "concentrated" vapour

$$\frac{2(p_\infty - p_o')}{p_o'} < \frac{2(p_\infty' - p_o'')}{p_o''}$$

but here again decomposition of initially adsorbed unmeasured H_2O_2 would tend to increase the percentage, so that while divergences between true and calculated values would be greater at high (1 mm.) than at lower pressures (0.5 mm.) (owing to the relatively larger amount of water present) they would be nearer the correct/

correct values than those indicated by the graph.

By employing equation (3) therefore and applying a small correction for the initial adsorption, which, as already stated, could not be measured accurately, the concentration of H_2O_2 in the vapour should, in the case of dilute solutions, be very little different from the actual concentration present, while in the case of more concentrated solutions the calculated percentage in the vapour would be expected to be somewhat lower than the actual concentration.

Exceptions to the latter statement would, however, be expected in three cases - i.e. in that previously mentioned (page 100) where the adsorption effect is exactly balanced by decomposition of initially adsorbed unmeasured H_2O_2; when the concentration is very high (about 100%), for, as adsorption in this case would be practically limited to H_2O_2, the calculated percentage should be higher than the true percentage; at very low pressures where the adsorption of H_2O_2 is comparable with that of water and the calculated percentage would again be expected to be high.

Results in accordance with these three postulates have actually been observed. It was noted that vapours drawn from a concentrated solution (98%) tended to give higher and higher values for the percentage as the initial pressure decreased from 1 mm. to 0.3 mm., in/

in the latter case the calculated concentrations sometimes being over 100%. In view of this it would appear that at initial H_2O_2 pressures of about 0.6 - 0.7 mm. the true and observed curves should be similar and the experimentally determined percentage be the true percentage - a supposition which from later results would appear to be correct. It was further observed that a more concentrated solution (in the region of 100%) gave values of slightly over 100% for the concentration of the vapour confirming the other suggestion in the last paragraph.

It should be emphasized that although these points have been discussed in some detail the actual pressure decrease due to adsorption was not large in comparison with the total change in pressure, e.g. a decrease of 0.01 mm. was observed for a 85% vapour which gave a final change in pressure of 0.45 mm. The effect, however, cannot be neglected altogether since it does have an influence on the percentage determinations and on the rate constants of the decomposition.

The causes for difference between the values calculated for the concentration of hydrogen peroxide in the vapour are therefore four:

(a) decomposition in the tubing between the reservoir and the reaction vessel;

(b) decomposition due to tap grease;

(c)/

(c) decomposition of the liquid in the reservoir while the vapour was being introduced;

(d) the "adsorption effect."

Each of these, in the experiments under consideration tend to make results obtained by the normal method less than those obtained in the presence of P_2O_5. The relative importance of each of these causes is somewhat difficult to judge, but, as the difference in the mean values obtained from the two methods is only about 2-3% (table IV), it would seem that the tap grease, at least, can have very little effect on the reaction.

It should be noted that the gauge employed in the above experiments was rather insensitive and was replaced after this set of experiments by a much more sensitive one, the calibration of which is tabulated on page 62. However, since the error in the above experiments was only of the order of 1%, it is evident that the results with P_2O_5 are slightly higher than those in its absence.

One very important observation made in the above experiments, and all subsequent ones, was that the reaction did not cease after about 20% of the peroxide present had decomposed. This is in disagreement with the observations of Elder and Rideal,[28] who found such a cessation in all their experiments, but agrees with the/

the observation of Kistiakowsky and Rosenberg,[29] who found no such cessation.

As the role of oxygen in the reaction is doubtful - one set of workers[28] suggested it inhibited the reaction, while another considered it had little or no effect[29] - the set of experiments discussed below were designed to elucidate any possible effect on the system.

First of all an experiment was performed with no added gas, and afterwards one was carried out where the hydrogen peroxide had, as nearly as possible within the limits of manipulation, the same partial pressure as in the first, but where a small amount of oxygen had been added. The results obtained, along with the calculated partial pressures of hydrogen peroxide and water are detailed in tables V and VI. The accompanying graph shows the time-pressure curves; the similarity between these curves is very striking. The same similarity is apparent in the curves obtained by plotting the partial pressure of hydrogen peroxide against time; indeed, in this case, only one line has to be drawn through the points. The added oxygen has therefore no effect on the rate of reaction under these conditions.

There are two possible explanations for this result, for it may be genuine, i.e. the oxygen has no effect on the reaction mechanism, or it may be due to two effects opposing each other and exactly cancelling out/

out. For instance if the reaction were a chain reaction, with an appreciable amount occurring in the gas phase and the chains breaking on the walls, a small amount of oxygen acting as an inert gas might decrease the probability of the chain carriers diffusing to the walls, and still not be sufficient to act as an efficient chain-breaking medium. If this were so, the addition of a small amount of gas would increase the rate of reaction appreciably, but this might be exactly balanced by an inhibiting effect of oxygen, so that the resultant rate would be unchanged. If such were the case, it should be easily checked by performing other experiments in the presence of small amounts of an oxygen-free inert gas, such as nitrogen, which would be expected to have no specific inhibiting effect on the reaction, but which would provide a medium capable of preventing, to a certain extent, diffusion to the wall, so that an increase in rate would result.

In table VII are tabulated the results of such an experiment, and by plotting these on the original graph it is immediately apparent that there is no measurable increase in rate.

It should be mentioned that no "infinity" readings were taken in the presence of any added gas, as it was feared that leaving the gas in the vessel overnight might have some undesirable effect on the surface, the nature/

nature of which must be kept as undisturbed as possible.[29] Consequently, the initial concentrations of hydrogen peroxide used in calculations of its partial pressures at the various time intervals during these runs were based on "blank" experiments - i.e. experiments without any added gas - carried out, as far as possible, under the same conditions. Thus, the accuracy claimed is only to within a few per cent. That these concentrations were fairly accurate, however, was shown later on the basis of an equation for the rate of reaction derived below.

The net result of this set of experiments was, therefore, that oxygen, in small amounts at any rate, had no inhibiting effect on the reaction. This is in agreement with the results of Kistiakowsky and Rosenberg, but in opposition to the view of Elder and Rideal that oxygen acts as an inhibitor to the reaction. If the equation derived by the latter workers were correct, i.e. if

$$\frac{dx}{dt} \propto \frac{1}{[O_2]}$$

where $\frac{dx}{dt}$ is the rate of reaction and $[O_2]$ the concentration of oxygen, it is easily shown that the rate of reaction for 0.55 mm. H_2O_2 in the presence of 8 mm. added oxygen should be practically zero.

The method adopted in initial experiments in the present/

present investigation was variation of one of the factors over as wide a range as possible, while the other variables were maintained constant within limits of manipulation of the apparatus. In the case of the variation of partial pressures of hydrogen peroxide, however, it was impracticable to consider rates at points where the partial pressures of oxygen and water were both constant, so, as it has been shown that oxygen, at least in small amounts, had no appreciable effect on the system, attention was concentrated on obtaining rates for various hydrogen peroxide pressures at a constant partial pressure of water vapour. By performing experiments with various initial pressures and various initial H_2O_2 concentrations, it was possible to vary the amount of H_2O_2 present at a given water concentration without adding water vapour to the system.

To this end several experiments were performed with initial total pressures ranging between 0.6 and 1.2 mm., which gave almost a 1 : 3 variation in the partial pressures of hydrogen peroxide at the partial pressure of water vapour chosen. These limits were imposed by two factors:

(a) It was not possible readily to obtain a higher pressure of vapour without heating the H_2O_2 solution in the reservoir, a procedure which had to be avoided, as/

as it would result in greater decomposition of the liquid and consequent dilution.

(b) The range was limited by the partial pressure of water chosen. The most convenient water vapour pressure over the above range was 0.35 mm., and for initial total pressures of less than about 0.5 mm. it was found that the time taken to reach this pressure during an experimental decomposition was inconveniently long. The lower limit at which rates were easily measurable was therefore in the region of 0.6 mm. initial total pressure.

The results obtained are detailed in table VIII and are represented by the accompanying graph showing rate against pressure of H_2O_2. The rates were determined by drawing tangents to the time - $[H_2O_2]$ curves at the appropriate points and confirmed by measuring the increase in pressure for two neighbouring points on the curve; these rates are considered accurate to approximately $\pm$ 0.0003 mm. per min. From the table and graph it is apparent that the rate is not proportional to the partial pressure of hydrogen peroxide, but to its square; the curve drawn on the graph which is in excellent agreement with the experimental points was actually calculated from the equation:

$$\text{Rate} = 0.055 [H_2O_2]^2 \quad \text{---------- (4)}$$

It/

It is interesting to note that in the few investigations into the thermal decomposition of hydrogen peroxide vapour so far published, the reaction has been considered to be either of the first order,[27] or of zero order.[28] With regard to solutions the same two orders have, so far as we know, been adopted in all cases except two, where a bimolecular equation has been proposed (a) for a solution decomposing on platinum-black while being irradiated by X-rays,[25] and (b) for moderately concentrated solutions (above ½ gm. mol. per litre) being decomposed by colloidal platinum[81] - reactions which do not seem to have any obvious connection with the thermal decomposition of the vapour. In the present case, for the conditions under consideration, there does not seem to be any doubt but that the decomposition is bimolecular with respect to the hydrogen peroxide concentration.

Mention has already been made of the fact that Elder and Rideal[28] considered inhibition by one of the products likely and suggested oxygen as the possible inhibitor. However, it has been shown above that oxygen, at least in small amounts, has no appreciable effect on the reaction, so the next set of experiments was devised as a means of testing the effect of the other product - water vapour - on the reaction.

For this purpose experiments were performed with no/

no added gas, and then in the presence of 1, 3, 5 and 10 mm. added water vapour (see Experimental, page 57). The results of these experiments were graphed in the usual manner - i.e. partial pressure of H_2O_2 against time - and rates at a constant partial pressure of H_2O_2 determined as before. The results obtained are shown in table IX and the accompanying graph. The 10 mm. run was abnormal and will be discussed later; it is therefore omitted from the table. From the figures quoted it is evident that water does have some inhibiting effect on the reaction, although the rate is not inversely proportional to the partial pressure of water vapour. The curve drawn on the graph - which fits the experimental points well - is the theoretical curve calculated from the equation:

$$\text{Rate} = \frac{0.0094}{(1 + 0.15\ [H_2O])^2} \quad \text{---------- (5)}$$

This equation was found to fit the points better than the equation

$$\text{Rate} = \frac{0.0094}{1 + 0.3\ [H_2O]} \quad \text{---------- (5a)}$$

although the latter fitted well for pressures up to 1 mm. In point of fact, it can be seen that the two expressions are really equivalent for low pressures of water vapour, for if $[H_2O]$ is less than 1 mm. the third term of the expanded denominator of (5) becomes negligible/

negligible in comparison with the other terms and equation (5) becomes:

$$\text{Rate} = \frac{0.0094}{1 + 2 \times 0.15 \left[H_2O\right]}$$

which is equation (5a).

From the above results we now have two equations for the rate of reaction i.e.

$$\frac{dx}{dt} = 0.055 \left[H_2O_2\right]^2 \quad \text{---------- (4)}$$

at 0.350 mm. partial pressure of H_2O ; and

$$\frac{dx}{dt} = \frac{0.0094}{(1 + 0.15 \left[H_2O\right])^2} \quad \text{--------- (5)}$$

at 0.400 mm. partial pressure of H_2O_2. Combining these equations we get an expression of the type:

$$\frac{dx}{dt} = \frac{k \left[H_2O_2\right]^2}{(1 + 0.15 \left[H_2O\right])^2}$$

We have two means of calculating k in this equation, for:

$$0.055 = \frac{k}{(1 + 0.15 \times 0.350)^2}$$

$$\therefore k = \underline{0.061}$$

and also

$$k \times (0.400)^2 = 0.0094$$

$$\therefore k = \underline{0.058}$$

The agreement between the values of <u>k</u> derived in these two ways is very good, and we may take the experimentally/

experimentally determined equation for the rate of decomposition of H_2O_2 vapour at low pressures in the silica vessel used as:

$$\frac{dx}{dt} = \frac{0.060\ [H_2O_2]^2}{(1 + 0.15\ [H_2O])^2} \text{ --------- } (6)$$

Several complete runs were examined by applying this equation, and that it does hold for a complete single run may be seen from the following set of tables.

Table XI.

Large Reaction Vessel. Temperature of Vessel = 80°C.
Temperature of Gauge = 25.5°C.
Initial Concentration of H_2O_2 = 68%.

Experimental.		Values from Smoothed Curve.					
Time	Pressure	Time	Pressure	$[H_2O_2]$	$[H_2O]$	Rate (exp.)	Rate(calc.
min.	mm.	min.	mm.	mm.	mm.	mm./min.	mm./min.
0	1.050	0	1.050	0.715	0.335	-	-
5	1.095	5	1.100	0.615	0.435	0.0175	0.0201
10	1.140	10	1.140	0.535	0.515	0.0136	0.0148
15	1.165	15	1.170	0.475	0.575	0.0115	0.0116
20	1.195	20	1.196	0.423	0.627	0.0090	0.0090
25	1.215	25	1.215	0.385	0.665	0.0073	0.0074
30	1.230	30	1.230	0.355	0.695	0.0064	0.0063
40	1.255	40	1.255	0.305	0.745	0.0046	0.0046
50	1.275	50	1.275	0.265	0.785	0.0034	0.0034
60	1.290	60	1.290	0.235	0.815	0.0027	0.0027
75	1.300	70	1.302	0.211	0.839	0.0020	0.0021
90	1.315	80	1.311	0.193	0.857	0.0018	0.0018
120	1.330	90	1.317	0.181	0.869	0.0014	0.0016
150	1.345	100	1.322	0.171	0.879	0.0011	0.0014
195	1.360	160	1.349	0.117	0.933	0.0008	0.0006
∞	1.400						

Table XII.

Large Reaction Vessel. Temperature of Vessel = 80°C.
Temperature of Gauge = 25.5°C.
Initial Concentration of H_2O_2 = 80%.

Experimental.		Values from Smoothed Curve.					
Time	Pressure	Time	Pressure	$[H_2O_2]$	$[H_2O]$	Rate (exp.)	Rate(calc.)
min.	mm.	min.	mm.	mm.	mm.	mm./min.	mm./min.
0	0.745	0	0.740	0.590	0.150	-	-
5	0.780	5	0.780	0.510	0.230	0.0140	0.0146
10	0.810	10	0.810	0.450	0.290	0.0114	0.0112
15	0.835	15	0.835	0.400	0.340	0.0088	0.0088
20	0.855	20	0.854	0.362	0.378	0.0070	0.0071
25	0.870	25	0.870	0.330	0.410	0.0060	0.0058
30	0.885	30	0.884	0.302	0.438	0.0048	0.0048
40	0.905	40	0.905	0.260	0.480	0.0036	0.0036
53	0.925	50	0.920	0.230	0.510	0.0027	0.0028
60	0.935	60	0.933	0.204	0.536	0.0022	0.0022
105	0.970	70	0.943	0.184	0.556	0.0017	0.0017
120	0.975	80	0.951	0.168	0.572	0.0014	0.0014
		90	0.958	0.154	0.586	0.0010	0.0012
		100	0.964	0.142	0.598	0.0009	0.0010

TABLE XIII.

Large Reaction Vessel. Temperature of Vessel = 81.3°C.
Temperature of Gauge = 25.4°C.
Initial Concentration of H_2O_2 = 84%.

Experimental.		Values from Smoothed Curve.					
Time	Pressure	Time	Pressure	$[H_2O_2]$	$[H_2O]$	Rate (exp.)	Rate(calc.)
min.	mm.	min.	mm.	mm.	mm.	mm./min.	mm./min.
0	0.741	0	0.741	0.622	0.119	-	-
5	0.782	5	0.781	0.542	0.199	0.0146	0.0167
10	0.819	10	0.815	0.474	0.267	0.0125	0.0125
20	0.864	15	0.843	0.418	0.323	0.0098	0.0096
25	0.878	20	0.863	0.378	0.363	0.0075	0.0077
30	0.889	25	0.878	0.348	0.393	0.0063	0.0065
43	0.914	30	0.890	0.324	0.417	0.0052	0.0056
52	0.930	40	0.912	0.280	0.461	0.0041	0.0041
60	0.942	50	0.930	0.244	0.497	0.0032	0.0031
75	0.960	60	0.944	0.216	0.525	0.0024	0.0024
90	0.970	70	0.955	0.194	0.547	0.0019	0.0019
105	0.978	80	0.963	0.178	0.563	0.0015	0.0016
∞	1.052	90	0.969	0.166	0.575	0.0012	0.0014
		100	0.974	0.156	0.585	0.0010	0.0012

TABLE XIV.

Large Reaction Vessel. Temperature of Vessel = 81.5°C.
Temperature of Gauge = 25.4°C.
Initial Concentration of H_2O_2 = 77%.

Experimental.		Values from Smoothed Curve.					
Time	Pressure	Time	Pressure	$[H_2O_2]$	$[H_2O]$	Rate(exp.)	Rate(calc.)
min.	mm.	min.	mm.	mm.	mm.	mm./min.	mm./min.
0	0.663	0	0.650	0.500	0.150	-	-
5	0.678	5	0.682	0.436	0.214	0.0105	0.0107
10	0.704	10	0.705	0.390	0.260	0.0082	0.0085
15	0.722	15	0.725	0.350	0.300	0.0070	0.0068
21	0.741	20	0.741	0.318	0.332	0.0058	0.0055
25	0.752	25	0.754	0.292	0.358	0.0045	0.0046
30	0.767	30	0.766	0.268	0.382	0.0040	0.0039
40	0.785	40	0.785	0.230	0.420	0.0028	0.0028
50	0.800	50	0.800	0.200	0.450	0.0024	0.0021
60	0.815	60	0.811	0.178	0.472	0.0018	0.0017
82	0.826	70	0.820	0.160	0.490	0.0014	0.0013
94	0.834	80	0.827	0.146	0.504	0.0012	0.0011
∞	0.900	90	0.832	0.136	0.514	0.0010	0.0010

TABLE XV.

Large Reaction Vessel. Temperature of Vessel = 81.5 C.
Temperature of Gauge = 25.5°C.
Initial Concentration of H_2O_2 = 84%.

Experimental.		Values from Smoothed Curve.					
Time	Pressure	Time	Pressure	$[H_2O_2]$	$[H_2O]$	Rate(exp.)	Rate(calc.)
min.	mm.	min.	mm.	mm.	mm.	mm./min.	mm./min.
0	0.378	0	0.367	0.308	0.059	-	-
5	0.382	5	0.382	0.278	0.089	0.0052	0.0045
10	0.392	10	0.393	0.256	0.111	0.0040	0.0038
15	0.404	15	0.402	0.238	0.129	0.0034	0.0033
25	0.415	20	0.410	0.222	0.145	0.0027	0.0028
30	0.422	30	0.424	0.194	0.173	0.0023	0.0021
40	0.433	40	0.436	0.170	0.197	0.0018	0.0016
50	0.445	50	0.445	0.152	0.215	0.0015	0.0013
60	0.452	60	0.452	0.138	0.229	0.0012	0.0011

TABLE XVI.

Large Reaction Vessel. Temperature of Vessel = 80°C.
Temperature of Gauge = 25.5°C.
Initial Concentration of H_2O_2 = 82%.

Experimental.		Values from Smoothed Curve.					
Time	Pressure	Time	Pressure	$[H_2O_2]$	$[H_2O]$	Rate(exp.)	Rate(calc.)
min.	mm.	min.	mm.	mm.	mm.	mm./min.	mm./min.
0	1.150	0	1.150	0.944	0.206	-	-
5	1.245	5	1.245	0.754	0.396	0.0290	0.0305
10	1.300	10	1.305	0.634	0.516	0.0198	0.0209
15	1.345	15	1.345	0.554	0.596	0.0148	0.0156
20	1.370	20	1.377	0.490	0.660	0.0118	0.0120
25	1.400	25	1.400	0.444	0.706	0.0097	0.0097
30	1.420	30	1.425	0.394	0.756	0.0078	0.0076
45	1.480	40	1.460	0.324	0.826	0.0055	0.0051
60	1.500	50	1.485	0.274	0.876	0.0040	0.0036
77	1.520	60	1.503	0.238	0.912	0.0028	0.0027
93	1.540	70	1.516	0.212	0.938	0.0022	0.0021
		80	1.527	0.190	0.960	0.0018	0.0017

The equation was first of all applied to runs where $[H_2O_2]_i$ was in the region of 0.6 mm. and the results are shown in tables XI, XII and XIII. The agreement between calculated and experimental values in these tables is excellent if one omits from consideration values during the first ten minutes or so: these are discussed below. In view of this close agreement the equation was then applied to runs with lower initial pressures (down to 0.3 mm. $[H_2O_2]_i$) and the results are shown in tables XIV and XV. The agreement here is still good although at the lower pressure not quite so good as previously. Finally, the run with the highest initial partial pressure of H_2O_2 so far obtained (about 0.95 mm.) was tested on the basis of the equation, and, here again, the agreement between calculated and experimental results is very good. In all cases, apart from the initial stages of some runs, the agreement between calculated and observed rates was within experimental error down to 0.1 mm. partial pressure of H_2O_2. Although concentrations of peroxide and water are given to the third decimal place in the above tables, it should be noted that the last figure may be unreliable. This will be especially so in the case of water, as any oxygen due to decomposition during or before introduction of the vapour to the vessel is somewhat variable and cannot be accounted/

accounted for, but the error will be very slight in the case of H_2O_2 concentrations, as these are calculated on experimentally determined percentages. However, as the partial pressure of water is only used in the term $(1 + 0.15 [H_2O])^2$ the partial pressure of water has little influence on the calculation. It appears therefore that equation (6), i.e.,

$$\text{Rate} = \frac{0.06 [H_2O_2]^2}{(1 + 0.15 [H_2O])^2}$$

is valid, under the present experimental conditions, over the $[H_2O_2]_i$ range 0.95 to 0.30 mm., over the $[H_2O_2]_m$ range 68 - 84%, and down to partial pressures of H_2O_2 of 0.1 mm. in any one run.

With regard to divergences between experimental and calculated rates during the first 5 -10 minutes of the reaction, it may be observed that the calculated rate is slightly higher than the experimental rate at high $[H_2O_2]_i$ but agreement between the two gets better as $[H_2O_2]_i$ is decreased. This can be accounted for satisfactorily on the basis of the adsorption effect previously discussed (pages 99-106), for, if adsorption of water occurs over the first ten minutes, or so, of the reaction, the observed rate will naturally be less than the true rate, as the pressure will not increase by the amount it should normally do in the absence of adsorption.

Further/

Further, as previously remarked, the true decomposition curve would be expected to correspond to the experimental curve at medium initial pressures of H_2O_2, while at lower pressures the experimental rates would be expected to be greater than the true rates on account of decomposition of initially adsorbed peroxide not measured by the system. The curves obtained for medium initial pressures (0.6 - 0.7 mm.) should therefore fit the equation for the rate of decomposition better than those for higher (up to 1 mm.) or lower initial pressures (< 0.5 mm.) This is in accordance with the experimental data given in tables XI to XVI where deviations are slight even over the entire range, although agreement between experimental and calculated values is noticeablybetter at medium pressures than at relatively higher or lower ones.

Times of half decomposition ($t_{\frac{1}{2}}$) for several runs carried out under comparable conditions were examined and are shown in table XVII.

TABLE XVII.

Large Reaction Vessel. Temperature of Vessel = 80°C.
Temperature of Gauge = 25.5°C.

$[H_2O_2]_i$ mm.	$t_{\frac{1}{2}}$ min.	$[H_2O_2]_i$ mm.	$t_{\frac{1}{2}}$ min.	$[H_2O_2]_i$ mm.	$t_{\frac{1}{2}}$ min.
0.944	21	0.660	23	0.550	28
0.798	20	0.622	33	0.380	28
0.715	29	0.590	35	0.275	49

It can be seen that, although the results are somewhat erratic, $t_{\frac{1}{2}}$ tends to increase as the initial concentration of H_2O_2 decreases. Now, it is universally agreed that the decomposition of H_2O_2 is a surface reaction (further evidence for this is given later) and it can be shown that this is the result one would expect for a bimolecular surface reaction retarded by one of the products, where the retardation is not strong.[82]

The equation for this type of reaction may be derived as follows. Let σ be the fraction of active surface covered with molecules of the reactant which is present at a pressure p_A and σ' the fraction covered by adsorbed product which is at a pressure p_P. Then the fraction of surface free from adsorbed molecules is $(1 - \sigma - \sigma')$, and equating the rate of condensation on the uncovered surface with the rate of evaporation from the covered surface (this must be so for equilibrium) we obtain:

$$k_1 p_A (1 - \sigma - \sigma') = k_2\sigma \text{ and } k_1' p_P (1 - \sigma - \sigma') = k_2'\sigma'$$

If we assume that the product is strongly adsorbed while the reactant is only weakly adsorbed - a state of affairs which we would expect to hold in the present reaction (see page 100) - the expression may be simplified:

$$\text{Covered Surface} = \sigma' = \frac{k_1' p_P}{k_2' + k_1' p_P}$$

$$\text{Uncovered Surface} = (1 - \sigma') = \frac{k_2'}{k_2' + k_1' p_P}$$

Now the rate, in a bimolecular reaction is proportional to the square of the amount of reactant condensing on the uncovered surface so, if the rate of reaction is $-\frac{dp}{dt}$:

$$-\frac{dp}{dt} = k \left\{(1 - \sigma') p_A\right\}^2$$

$$= \frac{k (k_2')^2 p_A^2}{(k_2' + k_1' p_P)^2}$$

$$= \frac{k p_A^2}{(1 + b' p_P)^2} \qquad \text{---------- (7)}$$

where $b' = \frac{k_1'}{k_2'}$. If a is the original amount of reactant (H_2O_2), x the amount transformed in time t (i.e. H_2O formed), and c the amount of retarding product (H_2O) originally present.

$$\frac{dx}{dt} = \frac{k (a - x)^2}{\{1 + b' (c + x)\}^2} \qquad \text{---------- (7a)}$$

$$= \frac{k \left[H_2O_2\right]^2}{(1 + b' \left[H_2O\right])^2} \qquad \text{---------- (7b)}$$

It may be observed that the equation (7b) derived by this treatment is the same as that derived empirically from the results, where the constants k and b' had the values 0.06 and 0.15 respectively.

This expression (7) may be expanded as follows:

$$-\frac{dp}{dt} = \frac{k p_A^2}{1 + 2 b' p_P + (b')^2 p_P^2}.$$

Now in the present case $\underline{b'}$ has the value 0.15 and, in the experiments we are considering, p_P is less than 1 mm. Under these conditions the term $(b')^2 \; p_P{}^2$ becomes negligible compared with $(1 + 2\, b' p_P)$. The equation may therefore be written

$$- \frac{dp}{dt} = \frac{k\, p_A{}^2}{1 + 2\, b' p_P}$$

$$\text{or} \quad - \frac{dp}{dt} = \frac{k\, p_A{}^2}{1 + b\, p_P} \qquad \text{----------} \qquad (8)$$

where $\underline{b} = \underline{2\, b'}$. If we express equation (8) in the nomenclature used in (7a):

$$\frac{dx}{dt} = \frac{k\, (a - x)^2}{1 + b\, (c + x)} \qquad \text{----------} \qquad (8a)$$

Equation (8a) can now be integrated yielding the equation:

$$k\, t = \frac{x}{a - x} \cdot \frac{1 + b\, (c + a)}{a} - b \log \frac{a}{a - x} \qquad \text{----} \qquad (9)$$

Therefore, if this expression were applied to a single run, it is evident that a straight line should be obtained by plotting $\frac{1}{t} \cdot \frac{x}{a - x}$ against $\frac{1}{t} \log_e \frac{a}{a - x}$. If we call $\frac{1}{t} \cdot \frac{x}{a - x}$, A, and $\frac{1}{t} \log_e \frac{a}{a - x}$, B, we can write (9) in the form

$$A = \frac{k\, a}{1 + b\, (c + a)} + \frac{a\, b}{1 + b\, (c + a)}\, B \qquad \text{------} \qquad (10)$$

According to (10), therefore, the slope of the line will be $\frac{a\, b}{1 + b\, (c + a)}$, and the intercept on the A axis/

axis will be $\frac{k\,a}{1 + b\,(c + a)}$. Knowing the slope of the line and the intercept on the A axis, the values of k and b can thus be calculated for that experiment.

As an example of the application of this equation, the results obtained by its use on one complete run are shown in table XVIII and the accompanying graph. For interpretation of the final column in the table see page 129 . It will be seen that the points vary somewhat but tend to decrease towards low concentrations of hydrogen peroxide. However, the line drawn on the graph appears to fit the points fairly well and from the intercept of this line on the $\frac{1}{t} \cdot \frac{x}{a - x}$ axis and its slope, the values calculated were

$$k = 0.056$$

$$b = 0.32$$

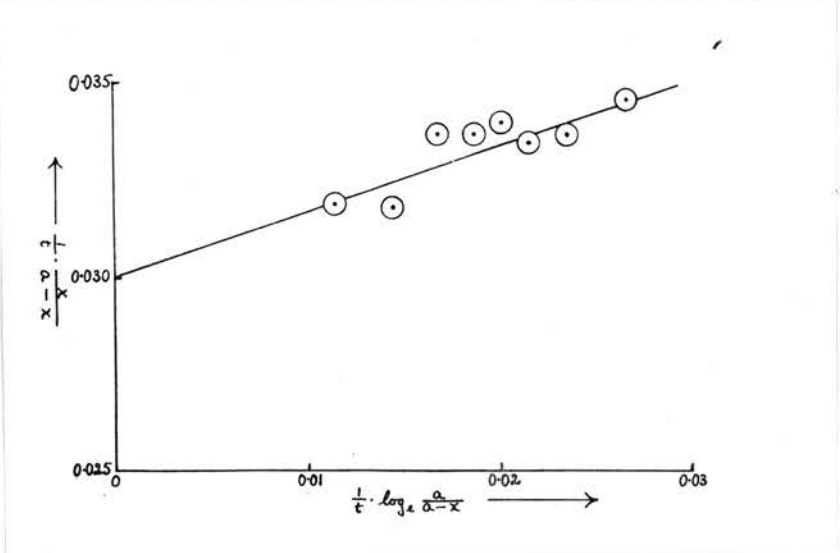
which is in satisfactory agreement with the values obtained empirically (0.06 and 0.3 respectively).

TABLE XVIII.

Large Reaction Vessel. Temperature of vessel = 80°C.
Temperature of Gauge = 25.5°C.
Initial total pressure = (c + a) = 1.05 mm.
Initial partial pressure of H_2O_2 = a = 0.715 mm.
Initial partial pressure of water = c = 0.335 mm.
x = $[H_2O]$ formed; (a - x) = $[H_2O_2]$ at time t.

x	(a - x)	t	$\frac{1}{t}\cdot\frac{x}{a-x}$	$\frac{1}{t}\log_e\frac{a}{a-x}$	k
mm.	mm.	min.			
0.292	0.423	20	0.0346	0.0263	0.0555
0.360	0.355	30	0.0337	0.0233	0.0550
0.410	0.305	40	0.0335	0.0213	0.0552
0.450	0.265	50	0.0340	0.0199	0.0566
0.480	0.235	60	0.0337	0.0185	0.0564
0.522	0.193	80	0.0337	0.0166	0.0570
0.544	0.171	100	0.0318	0.0143	0.0542
0.598	0.117	160	0.0319	0.0113	0.0553
				Mean -	0.0556

In calculation of k in table it is assumed that b = 0.30.



As mentioned above, the values of $\frac{1}{t} \cdot \frac{x}{a - x}$ were slightly variable and little removed from constancy over the entire range in any one run. This is exactly what one would expect on closer consideration of equation (9) when b is small, for as b gets smaller the slope of the line through the points obtained by plotting $\frac{1}{t} \cdot \frac{x}{a - x}$ against $\frac{1}{t} \log_e \frac{a}{a - x}$ should get smaller and smaller until, when b vanishes, it becomes zero, i.e. $\frac{1}{t} \cdot \frac{x}{a - x}$ becomes a constant. Thus for small values of b over the pressure range employed, any slight experimental error becomes greatly magnified (because the slope of the line is so small) on applying equation (9), so that this method is rather sensitive to apply to the present results. For a full direct confirmation of the equation it would be necessary to employ much higher pressures of H_2O_2 and to follow the decomposition curve over a much longer time range. Employment of higher pressures was avoided in the present work as it involved heating the solution with consequent greater risk of decomposition. Also the time range was limited by several factors, including the fact that towards the end of a run the pressure changes became so small that errors were liable to occur in reading the gauge.

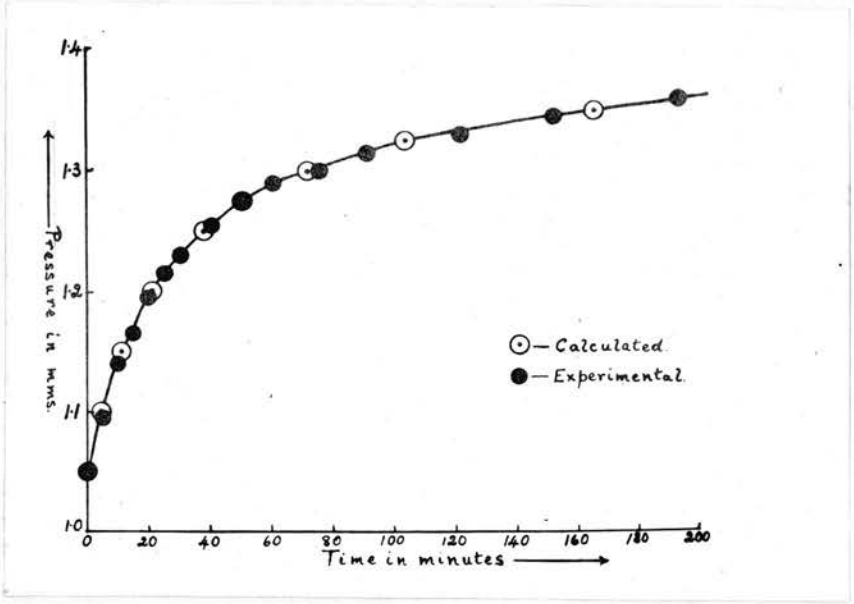
However, the existence of the b term can be confirmed in other ways. If we employ the experimentally determined value of b in equation (9) we should get a value/

a value for k which does not tend to decrease towards lower concentrations of hydrogen peroxide, as does $\frac{1}{t} \cdot \frac{x}{a - x}$ in the above table (XVIII). That this is the case is apparent from the last column of the table where k is calculated in each case from the equation:

$$k = \frac{1}{t} \cdot \frac{x}{a - x} \cdot \frac{1 + 0.3 \times 1.05}{0.715} - 0.3 \frac{1}{t} \log_e \frac{a}{a - x}$$

The value of k over the entire range is satisfactorily constant, confirming the fact that the decomposition does not quite follow the bimolecular law (i.e. $\frac{1}{t} \cdot \frac{x}{a - x}$ constant) but the modified bimolecular law as given by equation (9).

Still another confirmation is supplied by another method of application. From equation (10) above, knowing the values of k and b , it is possible to calculate back to the time-pressure curve. Two examples of this calculation are given in tables XIX and XX below, and the accompanying graphs compare the calculated curves with the experimental curves.


1·4
1·3
1·2
1·1
1·0
Pressure in mms.
0
20
40
60
80
100
120
140
160
180
200
Time in minutes
⊙— Calculated.
●— Experimental.

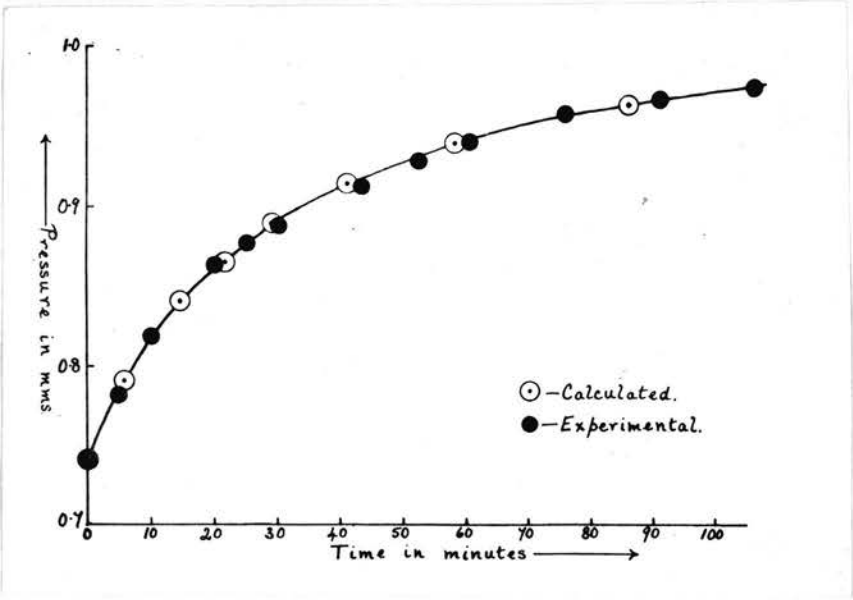

1·0
0·9
0·8
0·7
Pressure in mms
0
10
20
30
40
50
60
70
80
90
100
Time in minutes
⊙—Calculated.
●—Experimental.

TABLE XIX.

Initial total pressure = 1.05 mm.
Initial partial pressure of H_2O_2 = 0.715 mm.

$k = 0.056$. $b = 0.3$. $\frac{1 + b(c + a)}{a} = 1.84$. $c = 0.335$ mm.

Experimental		Calculated			
Time min.	Pressure mm.	x mm.	(a - x) mm.	Pressure mm.	Time min.
0	1.050	0.100	0.615	1.100	4.6
5	1.095	0.200	0.515	1.150	11
10	1.140	0.300	0.415	1.200	21
15	1.165	0.400	0.315	1.250	37.5
20	1.195	0.450	0.265	1.275	50
25	1.215	0.500	0.215	1.300	71
30	1.230	0.550	0.165	1.325	102
40	1.255	0.600	0.115	1.350	163
50	1.275				
60	1.290	N.B. Values of x in the above			
75	1.300	table were chosen arbitrarily,			
90	1.315	and the other values calculated			
120	1.330	therefrom.			
150	1.345				
195	1.360				

TABLE XX.

Initial total pressure = 0.741 mm.
Initial partial pressure of H_2O_2 = 0.622 mm.

$k = 0.057$. $b = 0.35$. $c = 0.119$ mm. $\frac{1 + b(c + a)}{a} = 2.03$.

Experimental		Calculated			
Time min.	Pressure mm.	x mm.	(a - x) mm.	Pressure mm.	Time min.
0	0.741	0.100	0.522	0.791	5.7
5	0.782	0.200	0.422	0.841	14.5
10	0.819	0.250	0.372	0.866	21.5
20	0.864	0.300	0.322	0.891	29
25	0.878	0.350	0.272	0.916	40.6
30	0.889	0.400	0.222	0.941	57.5
43	0.914	0.450	0.172	0.966	85
52	0.930				
60	0.942				
75	0.960				
90	0.970				
105	0.978				

The agreement between the experimental and calculated curves, as shown in the above results is remarkably good. This supports the various suggestions made previously during discussion of the adsorption effect in relation to initial pressures and observed rates.

Thus, there does not seem to be any doubt but that the decomposition of hydrogen peroxide vapour under the present conditions, i.e. low pressures in a silica vessel, is a surface reaction following the bimolecular law and being slightly retarded by water vapour, the equation governing the rate of reaction being:

$$\frac{dx}{dt} = \frac{k\,(a - x)^2}{\{1 + b\,(c + x)\}^2} \qquad \text{---------- (7a)}$$

the constants $\underline{k}$ and $\underline{b}$ having the average values 0.06 and 0.15 respectively for the silica vessel used. These values vary slightly over different runs presumably owing to change in the surface of the vessel.

There are several points of interest regarding this equation:

(1) Although it has been predicted by theory,[82,83] both on the basis of equilibrium considerations and the theory of absolute reaction rates, so far as can be ascertained, no other reaction following the full equation has been discovered. Only one example of a reaction which obeys a simpler form of the equation is/

is known to have been investigated - namely, the thermal decomposition of nitric oxide by platinum, a reaction which is retarded by oxygen.[84] The equation derived in this case was

$$\frac{dx}{dt} = \frac{k\,(a - x)^2}{x}$$

where the dehominator $(1 + b' x)^2$ has, owing to large adsorption of oxygen, reduced to the term x under the experimental conditions employed, i.e. at a platinum wire at temperatures above 1000°C.

(2) It is interesting to compare equation (7a) with that derived by Jeu and Alyea[64] for the decomposition of aqueous solutions of hydrogen peroxide in the presence of inhibitors. Their expression (see page 24) -

$$\frac{dx}{dt} = \frac{K\,(1 - x)}{k_2 + k_1 C}$$

where K, k_1, k_2 are constants, C is the amount of inhibitor and $(1 - x)$ the amount of reactant undecomposed at time t - is similar to (7a) except that it is derived from the unimolecular law. In deriving this equation they assume a fairly long chain, a supposition which, on the basis of Rice's work on the effect of dust particles,[15] does not appear to be valid. However, it should be pointed out that the same equation can be derived on the basis of a surface reaction, so it would appear that the function of an inhibitor is to render surfaces active for decomposition (e.g. of dust particles/

particles) less available for the hydrogen peroxide. Further, it has also been shown by Rice and co-workers that in an ordinary "dusty" solution the rate of decomposition approximates to unimolecular order.

The conclusion is, therefore, that here we have an example of an unusual type of reaction, the kinetics of which have been worked out by theory, but of which no example has so far been studied.

It would be expected that at higher pressures, where the amount of H_2O_2 present is relatively greater, this type would revert to a zero order reaction, and this may explain the order as determined by Elder and Rideal.[28] It would appear, however, that water and not oxygen, as postulated by these workers, is the retarding agent, and that the retardation is not quite so pronounced as given by the equation:

$$\frac{dx}{dt} = \frac{k}{x}$$

where x is the concentration of water vapour. With regard to their observation that the reaction ceased after 20% decomposition, it is here suggested that, in their experiments, the surface, after the usual practice of heating to 300°C, was in a state in which progressive adsorption of water, produced by the decomposition, reduced the surface available for decomposition to a value such that no appreciable decomposition was observable. In the present experiments the rates, being/

being proportional to the square of the H_2O_2 concentration and decreasing with increasing H_2O, became rapidly smaller: at about 20% decomposition the rate curve did, in fact, show usually a noticeable inflexion.

In the case of the pressure-time curves for experiments performed in the presence of relatively high pressures of water vapour (about 10 mm.) a pronounced periodic alteration in pressure was observed. The results obtained in one such experiment are detailed in table XXI and are represented by the accompanying graph.

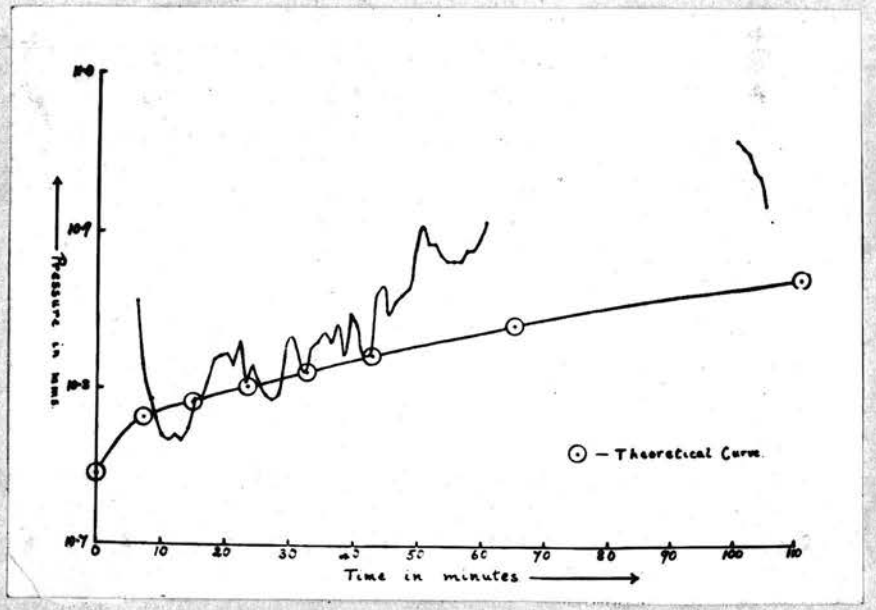

Pressure in mms
10-6
10-7
0
10
20
30
40
50
60
70
80
90
100
110
Time in minutes
⊙ — Theoretical Curve.

Table XXI.

Large Reaction Vessel. Temperature of Vessel = 81.80°C.
Temperature of Gauge = 26.20°C. $[H_2O_2]_m$ = 75%.
Pressure of Water Vapour Added = 10 mm.

Time min.	Pressure mm.	Time min.	Pressure mm.	Time min.	Pressure mm.
0	0.745	26	10.796	47	10.860
6	10.856	27	10.793	48	10.864
7	10.815	28	10.796	49	10.889
8	10.793	29	10.826	50	10.904
9	10.781	30	10.834	51	10.893
10	10.770	31	-	52	10.893
11	10.767	32	10.811	53	10.886
12	10.770	33	10.826	54	10.882
13	10.767	34	10.830	55	10.882
14	10.774	35	10.837	56	10.882
15	10.793	36	10.830	57	10.889
16	10.793	37	10.841	58	10.889
17	10.804	38	10.822	59	10.896
18	10.819	39	10.848	60	10.907
19	-	40	10.841		
20	10.822	41	10.822	99	10.960
21	10.815	42	10.822	100	10.956
22	10.830	43	10.860	101	10.952
23	10.804	44	10.866	102	10.941
24	10.815	45	10.848	103	10.937
25	10.804	46	10.856	104	10.919

Ten mm. of water vapour were introduced between 0 and 6 min. During these 6 min. the H_2O_2 is assumed to decompose at its normal rate, and on the graph the pressure is given as 10.745 mm. at 0 min. The theoretical curve on the graph was calculated from the integrated form of the full expression:

$$\frac{dx}{dt} = \frac{k(a-x)^2}{\{1 + b'(c+x)\}^2}$$

i.e.:

$$kt = A\frac{x}{a-x} - B\log\frac{a}{a-x} + Cx$$

where $A = \dfrac{1 + b'(2a + 2c + a^2b' + b'c^2 + 2ab'c)}{a}$;

$B = 2b'(1 + b'c + b'a)$;

$C = b'^2$;

and k and b' had the values 0.06 and 0.15 respectively.

Here a periodic actual decrease in pressure is to be observed, which is, of course contrary to the normal increase due to the decomposition. The magnitude of this decrease and of the periodic increases which follow and precede it were much greater than could be accounted for on the basis of any temperature alterations in the system. At the pressure used (11 mm.) the increase in pressure at, for example, time 42 - 44 min. would correspond, on the basis of Boyle's and Charles' Laws, to an increase of 1.5°C, far outside the experimental variations in the thermostat temperature. Indeed, careful observation showed that decreases frequently occurred while the thermostat temperature was actually rising; it is therefore to be concluded that accidental temperature variations of the system as a whole cannot be responsible. This was confirmed by an experiment carried out with 10 mm. of water vapour in the vessel, but no H_2O_2. It was observed that after about 7 min. the pressure fell to a steady value, and, as expected, no periodic behaviour was observable. Furthermore, that the phenomenon is not restricted to temperatures in the region of 80°C was demonstrated by an experiment carried out at 120°C, which gave essentially the same result as above.

The same phenomenon was observed at lower pressures of water vapour although it was much less pronounced (e.g. it just becomes apparent in the range 5 - 7 mm. added/

added water vapour), and it seems obvious that the periodic variation must be due to circumstances connected with the presence of water. Periodic variations in the rate of decomposition of hydrogen peroxide have been previously reported for solutions decomposing at various surfaces, e.g. mercury,[24] but this does not seem to have any obvious connection with the present observations. With regard to the decomposition of the vapour, however, it has been reported[28] that a mercury surface does not exert a periodic action.

The present example is of unusual interest in that an actual decrease in pressure is recorded, corresponding to an apparent negative rate of reaction. At the relatively high pressure of water vapour employed the amount of water adsorbed on the walls of the vessel will be much greater than is usually found for the normal decomposition at the low pressures previously discussed. The pressure of H_2O_2 remained less than 1 mm. as before. Thus, as there is no evidence for complex formation between the H_2O_2 and the water in the vapour,[28] it seems likely that the periodic effect in the presence of water vapour is not due to a gas-phase reaction but is one which, as before, is dependent on the conditions at the surface.

This is in agreement with the view of Hedges and Myers[85] that periodicity is 'associated with surfaces and is probably a function of surface energy.' These authors/

authors also state that the cleaning of reaction tubes is of importance and that small quantities of various substances can cause periodicity, although in several cases these substances have not been identified. However, it would appear that, in the present case, water vapour is the cause of the periodicity.

It is obvious that, in such a periodic variation, equilibrium processes cannot be involved at all stages of the reaction. The previous theory of the surface decomposition is based on the equilibrium between adsorbed and gas- phase H_2O_2 - i.e. if areas were imagined to be "cleared" by, say, the normal heat of reaction causing local evaporation, such "clearings" and subsequent condensations must reach an equilibrium condition resulting in a smooth curve of decomposition.

The effect of added water vapour is normally to reduce the rate of reaction by the factor $\frac{1}{(1 + 0.15[H_2O])^2}$ this representing the decrease in surface available for adsorption and ultimate decomposition of the H_2O_2. It might be thought possible that at 10 mm. water vapour pressure the number of available centres would become negligible (any heat effect would, of course, be less than before) and the kinetics then not predictable on a statistical basis. The rate, however, as given by a smooth curve drawn through the averages of the extremes of pressure is slightly higher

than/

than that expected according to the relation holding at lower pressures (see graph for table XXI), but is similar. It would appear, therefore, that the main picture remains as before, but is obscured by some factor depending on the high water vapour pressure.

If the added water merely covers more of the "active centres" for decomposition, there is no obvious reason why the velocity should depart from the normal in the uncovered areas. The periodic variation must thus be connected with the areas "covered" by water. If this is so, the rate of reaction should be above that expected on the basis of the formula, in agreement with the results obtained.

Considering first the pressure decreases, it would appear that there are two possible reasons for this. Water vapour, in contrast to other gases, such as N_2, etc., has been considered to form, at higher pressures, a multimolecular surface layer.[86] When the pressure decreases, therefore, one of the possible processes occurring is removal of some gaseous H_2O_2 by solution in this layer; the other possible process is adsorption of H_2O and H_2O_2 on areas which have been "cleared" by desorption as described below. This, in turn, is followed by an increase in pressure due to decomposition and desorption (vide infra) and so the cycle is repeated.

With regard to the increases in pressure, it is immediately/

immediately obvious that these cannot be due entirely to decomposition of the H_2O_2, as the summation of all these increases over only the first 60 minutes of the reaction is greater than can be accounted for on the basis of the amount of H_2O_2 present. The increases cannot therefore be due to a mechanism of, say, a thermal chain reaction of the unstable non-stationary type, which might be envisaged as auto-catalytic and increasing by virtue of the heat of decomposition made available at earlier stages. They must therefore be accounted for by a non-equilibrium condition resulting in the expulsion of H_2O_2, H_2O and O_2.

As described in the Introduction (pages 19 - 27), the accepted theory of the decomposition of H_2O_2 in aqueous solution involves the presence of solid-liquid interfaces (e.g. at the surfaces of dust particles and at the walls of the vessel). In these cases the solution layers envisaged above must be involved. If the reaction is truly a surface one, then some separation of H_2O_2 from the solution must take place. It has been observed, also, that freezing out of H_2O_2 in aqueous solutions is a matter of some difficulty (pages 85-86, see also reference 77), and although the cases are not quite parallel some degree of separation must be involved in both. If solution of H_2O_2 in the adsorbed water layer is followed by displacement of water from the surface by H_2O_2, a preferential adsorption of H_2O_2 to/

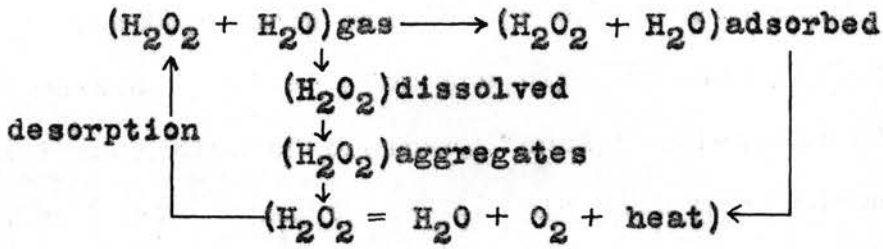
to H_2O_2, forming an aggregate of H_2O_2 molecules, may occur, corresponding to rapid crystallisation of H_2O_2 from a supersaturated solution. The subsequent decomposition of an adsorbed H_2O_2 aggregate might then be in the nature of an incipient explosion, either by a chain reaction or a heat effect. The tendency for concentrated H_2O_2 solutions to explode has already been recognised.[78]

These remarks are in agreement with an explanation suggested by Rice[15] for the high quantum yields obtained on irradiation of ordinary "dusty" solutions of H_2O_2. He suggested that the H_2O_2 molecules were adsorbed in aggregates on dust particles, absorption of one quantum of light energy decomposing one molecule, and this causing decomposition of the whole aggregate.

The effect on the surface in the decomposition of the vapour would be different from that in solution, in that, in the latter, heat effects would be dissipated by the large amount of water present, and the amount of H_2O_2 available for concentration at the surface limited by diffusion to the "active centres" from the main body of the solution. In the present case, therefore, some of the H_2O_2 must be taken to decompose, but to account for the pressure increases observed this decomposition must be accompanied by temporary removal from the neighbouring surface of some water and H_2O_2, as well as the oxygen formed. It would then be expected that the rate/

rate of reaction would be greater at the beginning of the run but fade off towards the end. From the experimental results it can be seen that the first of these criteria is satisfied, but the reaction has not been followed sufficiently far to observe the second.

This explanation, therefore, does appear to be in accordance with the recorded data, and may be summarised as follows:



Full confirmation of this theory would require further investigation. It is suggested that a good method of recording the results would be to have a mirror attached to the pointer of the gauge, the path of a spot of light reflected from this mirror being recorded on photographic paper on a rotating drum. This would be more accurate for observation of the actual periodic variations, for when readings are taken every minute, as in the present case, the actual trough or crest of the "wave" may be missed.

This example of periodicity is especially worthy of consideration, as the conditions under which it was observed differ completely from those under which the periodic decomposition of hydrogen peroxide has so far been/

been investigated,[24] and its investigation might lead to a clarification of the mechanism of periodic reactions. No full investigation was possible during the time of the present research.

On completion of these sets of experiments, a short study of the effects, on the decomposition, of various gases was carried out. Several experiments were performed, first of all with various pressures of added nitrogen, following the procedure detailed on pages 60 - 61. As it had been shown that small quantities of oxygen did not have any appreciable effect on the reaction, another set of experiments were performed employing higher pressures of oxygen. To complete the series two experiments with small amounts of hydrogen and one with carbon dioxide were carried out. The results of all these experiments are tabulated in table X (page 75) and those performed under comparable conditions are represented by the accompanying graph. In general, it is evident that there is a decrease in the rate of reaction as the concentration of added gas increases. It should be mentioned that the H_2 and CO_2 experiments are not strictly comparable with the others, as they were performed after concentration of the H_2O_2 solution in the reservoir and, also, higher initial pressures were used. The results are compared, in each case, with an experiment with no added gas performed at about the same time and under the same conditions./*

conditions. The rates for each set are compared at partial pressures of H_2O_2 and H_2O as constant as possible within the limits of manipulation of the apparatus.

The relative rate of diffusion of a particle A through a gas X is given by the equation:[87]

$$D_X = \sqrt{\left(\frac{1}{M_A} + \frac{1}{M_X}\right)} \sigma_{AX}^{-2} [X]^{-1}$$

where M_A = molecular weight of diffusing particle;

M_X = molecular weight of gas X;

σ_{AX} = sum of radii of diffusing particle A and gas molecule X;

and $[X]$ = pressure of gas X.

For a mixture of H_2O_2 with other gases (M_1, M_2, etc.) the time of diffusion through a certain distance is taken as:

$$t = \frac{1}{D_{H_2O_2}} + \frac{1}{D_{M_1}} + \frac{1}{D_{M_2}} + \cdots\cdots ,$$

and the relative rate of diffusion is then:

$$D = \left(\frac{1}{D_{H_2O_2}} + \frac{1}{D_{M_1}} + \frac{1}{D_{M_2}} + \cdots\cdots\right)^{-1}$$

This formula may be applied when the distribution of diffusing particles remains unaltered throughout the reaction vessel.

Using the following data it is possible to evaluate D for any pressure of added gas:

$\sigma_{H_2O_2}$/

$\sigma_{H_2O_2} = 3 \times 10^{-8}$ cm. (An approximation from the known structure); $\sigma_{H_2O} = 2.6 \times 10^{-8}$ cm.; $\sigma_{O_2} = 2.9 \times 10^{-8}$ cm.; $\sigma_{N_2} = 3.1 \times 10^{-8}$ cm.; $\sigma_{H_2} = 2.3 \times 10^{-8}$ cm.; $\sigma_{CO_2} = 3.2 \times 10^{-8}$ cm.

Concentrations [X] were expressed in millimetres.

It can then be shown that the relative rate of diffusion of H_2O_2 in the presence of a certain amount of nitrogen is very close to that in the presence of the same amount of oxygen, e.g. values for D for 169 mm. are:

$$D = 1.67 \times 10^{12} \text{ for } O_2;$$

$$\text{and } D = 1.62 \times 10^{12} \text{ for } N_2;$$

while for 76 mm.:

$$D = 3.69 \times 10^{12} \text{ for } O_2;$$

$$\text{and } D = 3.58 \times 10^{12} \text{ for } N_2.$$

Therefore, if the observed decrease in rate of reaction with increasing concentration of added gas is due to the decrease in diffusion of H_2O_2 from the bulk of the vapour to the wall, with consequent decrease in the H_2O_2 available for adsorption and subsequent decomposition, it is evident that the rates should decrease by practically the same amount in the presence of added oxygen as in the presence of the same amount of nitrogen. That this holds in the present case is evident from the graph of table X, where the points for O_2 and N_2 are reasonably close to the same curve.

Further/

Further, unless diffusion of H_2O_2 to the wall is the rate-determining step, which seems unlikely under the present conditions (low pressures and high H_2O_2 concentrations), it would be expected that the rate of reaction would be constant until a certain pressure of added gas is reached, and would decrease with increased pressure when the rate of diffusion becomes a factor in the determination of the rate of reaction. In the case of nitrogen and oxygen it can be seen that the reaction rates are unaffected up to about 10 mm. added gas and then decrease, which is in agreement with the above postulate.

Examining the experiments carried out in the presence of hydrogen and carbon dioxide, it is evident that 2 mm. of H_2 and 11.4 mm. of CO_2 have little, if any, effect on the reaction rates. For 10 mm. of H_2 it is evident, however, that the rate is definitely below that in the CO_2 experiment. This is contrary to what one would expect on the basis of the diffusion theory, as hydrogen should have the least effect of any of the gases, e.g. for 10 mm.:

$$D = 9.74 \times 10^{13} \quad \text{for } H_2;$$

$$\text{and } D = 2.20 \times 10^{13} \quad \text{for } CO_2.$$

As the decrease in rate of reaction cannot be accounted for by the diffusion theory, it would appear, therefore, that hydrogen has some effect on the reaction mechanism/

mechanism at the temperature employed; perhaps in some such manner as envisaged by von Elbe and Lewis[71] (see page 30). Elucidation of this point would require further investigation.

Experiments performed in the presence of 500 mm. added gas gave rather erratic results. One with 500 mm. N_2 gave a reaction rate of 0.0021 mm./min. at 0.400 mm. H_2O_2 concentration, which fits in fairly well with what would be expected on the basis of the diffusion theory. Another, carried out under apparently the same conditions, gave a rate of about 0.0050 mm./min., while one with 500 mm. O_2 gave a rate of 0.0030 mm./min., both at 0.400 mm. H_2O_2 concentration. It should be pointed out that determination of rates in these cases was difficult, as it appeared that periodicity was again becoming observable. However, the evidence for this is not conclusive, as the periodic variations were of the order of the "temperature corrections" for thermostat variations, so this point also might repay further investigation.

As it has been reported that the temperature coefficient of the thermal decomposition of hydrogen peroxide vapour is almost negligible,[29] the next set of experiments dealt with the variation of reaction rate with temperature. For this purpose, several experiments were performed at temperatures between 15°and 140°C. In this case the thermostat round the reaction vessel was/

was replaced by the electric heater(page 52), and the temperature adjusted by means of a hand rheostat and an accurate thermometer. The $[H_2O_2]$-time curves were plotted as before, and the reaction rates at a fixed partial pressure of H_2O_2 determined. The results are shown in table XXII and the accompanying graph. As all the experiments were not performed with the same initial pressure of H_2O_2 the rates were determined at a constant partial pressure of H_2O_2 and corrected for the additional amount of water present, on the basis of the equation for the rate of reaction; the corrections, however, were small in all cases.

Table XXII.

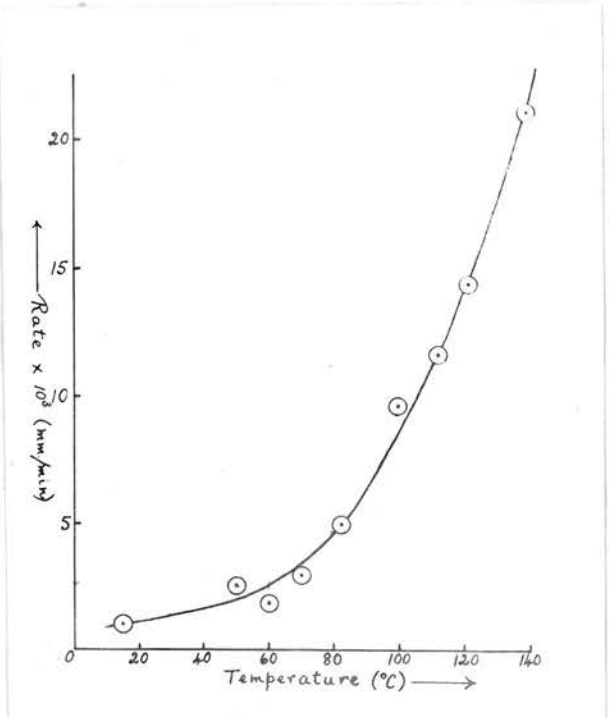
Large Reaction Vessel. Temperature of Gauge = 25.0°C.

$[H_2O_2]$ = 0.205 mm.

Temperature of Vessel. °C	$[H_2O_2]_i$ mm.	Rate(exp.) mm./min.	Rate(corr.) mm./min.
15	0.562	0.0013	0.0010
50	0.620	0.0027	0.0025
60	0.640	0.0020	0.0018
70	0.690	0.0030	0.0029
82	0.856	0.0050	0.0049
99	0.940	0.0095	0.0095
111	0.920	0.0115	0.0115
120	0.664	0.0146	0.0142
137	0.870	0.0210	0.0208

Rates in last column corrected to;

$[H_2O]$ = 0.745 mm.



It can be seen that the rate varies very little over the temperature range 15 - 60°C, but above 60° it increases considerably. From the graph obtained it is possible to calculate the apparent heat of activation of the reaction over several temperature ranges. The heat of activation at any temperature is given by the equation:

$$\text{Rate} = ke^{-\frac{E}{RT}},$$

where k is a constant depending on the concentration; e is the natural base of logarithms; E is the apparent energy of activation; R is the gas constant; and T is the absolute temperature. Thus, if we take rates at two different temperatures, all other conditions being the same we get:

$$\text{Rate}_1 = ke^{-\frac{E}{RT_1}}$$

$$\text{and} \quad \text{Rate}_2 = ke^{-\frac{E}{RT_2}}$$

Then

$$\frac{\text{Rate}_1}{\text{Rate}_2} = e^{\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)},$$

and hence we can determine E over the range chosen. In this way E was determined for several ranges, the values obtained being given in the following table.

Table XXIII.

Temperature Range °K	Apparent Heat of Activation cals.
288-333	3800
333-353	7550
353-373	8050
373-393	7600
393-413	6700

Mean E over range 333 - 413°K = 7500 cals.

In/

In the above determination it was not found practicable to exceed 140°C, as the rates above that temperature became too rapid to be easily measurable by the method employed. This set of experiments ~~were~~ was performed with the most concentrated solution of hydrogen peroxide so far used (analysis with permanganate gave a figure of 100%), and a difficulty encountered in these runs was that the percentage of H_2O_2 in the vapour, as calculated from the infinity reading, was frequently over 100%. The reason for this has already been discussed under the "adsorption effect" (pages 99 - 106).

It should be noted that the apparent energy of activation is not constant over the range employed. In the region 15 - 60°C, the value obtained was 3800 cals., while above 60°C the average value was 7500 cals. This is what would be expected if a gas-phase reaction were becoming appreciable, the smaller value being that for the surface reaction and the upper one taking into account the gas-phase reaction. The appearance of a gas-phase reaction above 60°C might also account for the apparent effect of hydrogen on the reaction. If the gas-phase reaction, under the conditions employed, is bimolecular, there would be little change in the equation derived for the rate of reaction. This point also requires further investigation.

It is interesting to compare the above values with that obtained by Allmand and Style,[18] who found the heat

of/

of activation for the photochemical decomposition in solution to be about 5500 cals.

For a final series of experiments the reaction vessel used up to this point (volume = 31.35 ml.) was replaced by the small reaction vessel (volume = 21.74 ml.). After several runs the results became reproducible, and an example of a determination carried out with this apparatus is given in table XXIV.

Table XXIV.

Small Reaction Vessel. Temperature of vessel = 83.0°C.
Temperature of Gauge = 25.0°C.

Time min.	Pressure mm.	Time min.	Pressure mm.
0	0.756	21	1.170
1	0.830	30	1.212
2	0.895	46	1.243
5	1.010	52	1.251
7	1.057	∞	1.412
11	1.121		

There are several points with regard to these results which require consideration. The most obvious is that the percentage of H_2O_2 in the vapour, at the given gaseous pressure, as calculated from the "infinity" reading, is in the region of 170%. Experiments with the other vessel carried out just prior to this gave figures of 98 - 99%, which is what one would expect, from the concentration of the solution. It might seem, at first sight, that this abnormal result might be due to

some/

some defect in the apparatus, such as a leak; but this cannot be, for the increase of pressure over the first ten minutes (at 10 min. it gives a concentration figure of approximately 100%) is much greater than that occurring over 20 hours, i.e. between the last reading and the "infinity" reading, where the pressure increase is only 0.161 mm. These figures were reproducible and so it would appear that the effect is genuine. This result again demonstrates the surface nature of the reaction, for, if the reaction were in the gas-phase, the concentrations obtained in the two vessels should be the same, and the total rate should be less in the smaller vessel.

An attempt was made to deduce the order of the reaction from these results. The rates of decomposition were determined in the usual manner at several time intervals in the range 0 - 10 min. The concentrations of H_2O_2 at the intervals chosen were then calculated on the basis of the initial concentration being 100%. As it had been shown earlier that the retardation by water was small, this was neglected. With these assumptions it was found that the rate was approximately proportional to the concentration of H_2O_2 present, i.e. the apparent order of the reaction is the first.

Now, it is evident from the results for the percentage H_2O_2 quoted above that considerable adsorption of H_2O_2 must occur on the surface of this vessel. If the surface were fully saturated, an apparent order of zero would/

would be obtained, irrespective of the true order of the reaction.[82] It has been shown above that, for a surface which is not saturated, the order of reaction is the second. Therefore, at an intermediate stage the reaction should be approximately unimolecular. This may be the state of affairs existing here.

It has recently been shown that potassium chloride promotes recombination of OH radicals,[88] so an attempt was made, using the small reaction vessel, to determine the rate of reaction with the surface covered with KCl. It was hoped, in this way, to gain some information about the reaction mechanism. The vessel was coated by washing out with a 10% KCl solution and drying by evacuation with the oil-pump. The results were inconclusive, however, for the rate in the presence of KCl was slighly faster than that in its absence (pressure increases of 0.148 mm. and 0.139 mm. respectively were obtained during corresponding time periods in comparable runs), but this increase may be accounted for by the introduction of fresh surface - in the form of KCl - into the vessel.

Finally an attempt was made to evaluate an equation deduced from the theory of absolute reaction rates for a bimolecular surface reaction inhibited by one of the products, and to compare it with the results obtained above. The equation obtained above for the rate of reaction in the large silica vessel was (page 124);

$$-\frac{dp_A}{dt} = \frac{0.06\ p_A^2}{(1 + 0.15p_p)^2}$$

If we assume, for simplicity, that we are dealing with 1 mm. of H_2O_2 in the absence of water, the denominator $(1 + 0.15p_p)^2$ becomes unity, and we get:

$$-\frac{dp_A}{dt} = 0.06 \text{ mm./min.}$$

This can easily be reduced to the number of molecules per 31.35 ml. reacting per second and, knowing the approximate apparent surface area of the vessel (54 sq. cm.), to the number of molecules reacting per sq. cm. per second. The value obtained in this case is 15.9×10^{12} molecules $cm.^{-2}$ $sec.^{-1}$

Now the equation derived for such a reaction from theory (reference 83, p.385) is:

$$v = \tfrac{1}{2}s\ \frac{c_g^2 c_s}{1 + A_p c_{gP}}\ h\ \frac{kT}{h}\ \frac{f_\ddagger}{F_g^2 f_s}\ e^{-\varepsilon_o/kT}$$

where v = rate of reaction;

s = total number of possible sites adjacent to any reaction centre;

c_g = concentration of reactant in the gas phase;

c_s = number of reaction sites per square centimetre of surface;

c_{gP} = concentration of inhibitor in the gas phase;

$f_\ddagger$ = partition function for activated complex;

F_g = partition function of the reactant for unit volume;

f_s/

f_s = partition function for reaction sites;

e = natural base of logarithms;

ε_o = heat of activation at 0°K:

k = Boltzmann's constant;

T = Absolute temperature;

and A = an expression of the type $\frac{f_{aP}}{F_{gP} f_s} \cdot e^{-\varepsilon/kT}$, which need not concern us here, as we are considering the case where c_{gP} is zero, and thus the term $A_p c_{gP}$ vanishes.

By assuming $\frac{f_\ddagger}{f_s}$ to be unity (reference 83, p.387), and substituting for F_g the expression in reference 83, p. 374, we get the final expression:

$$v = c_g^2 c_s \cdot \left(\frac{\sigma}{\sigma_\ddagger}\right)^2 \frac{\frac{1}{4} s^3 h^{11}}{64\pi^4 (8\pi^3 ABC)(2\pi m)^3 (kT)^6} \cdot e^{-\varepsilon_o/kT}$$

where $\sigma, \sigma_\ddagger$ = symmetry numbers of reactant and activated complex, respectively;

h = Planck's constant = 6.55×10^{-27};

A, B, C = the three moments of inertia of the reactant;

m = mass of a molecule of the reactant.

From published data the following values may be inserted in the above equation for H_2O_2:

$c_g = 2.74 \times 10^{16}$ molecules (1 mm. at 355°K);

$c_s \simeq 10^{15}$ sites per sq. cm. (reference 83, p.374);

$s \simeq 4$ (see reference 83, p.374);

$\sigma = \sigma_\ddagger$ (see reference 83, p. 180);

A/

$A = 33.2 \times 10^{-40}$ gm. cm.^{2} (reference 53);

$B = 33.5 \times 10^{-40}$ gm. cm.^{2} (reference 53);

$C = 2.7 \times 10^{-40}$ gm. cm.^{2} (reference 53);

$m = \frac{34}{6.06 \times 10^{23}}$ gm. ;

$T = 355^{\circ}K$; $k = 1.37 \times 10^{-16}$ ergs/degree;

and $\frac{\varepsilon_0}{k} = \frac{E_0}{R}$

where E_0 = heat of activation per mole at $0^{\circ}K$;

R = gas constant = 1.98 cals./degree.

If the experimental heat of activation were constant over a wide range of temperature, this might be substituted for E_0. (See reference 83, p.381). However, as shown in the above results the energy of activation changes at about $60^{\circ}C$ from 3800 cals. to 7500 cals. We can substitute both these values for E_0 and evaluate the equation in each case. We then get:

$v = 9.7 \times 10^{12}$ molecules cm.$^{-2}$ sec.$^{-1}$ (3800 cals.)

$v = 5.13 \times 10^{10}$ molecules cm.$^{-2}$ sec.$^{-1}$ (7500 cals.)

The first of these is in good agreement with the experimental result (15.9×10^{12} molecules cm.$^{-2}$ sec.$^{-1}$) and this calculation, therefore, is in confirmation of the suggestion made earlier that the value of the energy of activation over the range 15 - $60^{\circ}C$ refers to the pure surface reaction, while above $60^{\circ}C$ some disturbing factor is becoming appreciable.

The values obtained finally for the rate of reaction are therefore:

<u>Experimental</u> $v = 15.9 \times 10^{12}$ molecules H_2O_2 cm.$^{-2}$ sec.$^{-1}$

<u>Calculated</u> $v = 9.7 \times 10^{12}$ molecules H_2O_2 cm.$^{-2}$ sec.$^{-1}$

SUMMARY.

1. A convenient method for the preparation of small quantities of chemically pure very concentrated aqueous solutions of hydrogen peroxide has been devised.

2. The composition of the vapour drawn from a solution of known strength at room temperature was found to be substantially in agreement with that expected from published data. Several points regarding adsorption of H_2O and H_2O_2 on the walls of the reaction vessel, in which the decomposition was investigated, and the effect of this on the experimental values for the concentration of H_2O_2 in the vapour and on the apparent reaction rates have been discussed.

3. The decomposition of hydrogen peroxide vapour in a silica vessel at low pressures (less than 1 mm.) has been investigated, mainly at 80°C, but also over the temperature range 15 - 140°C.

4. Oxygen, at low pressures (less than 10 mm.), was found to have no appreciable retarding effect on the reaction; the rate of reaction was found to be proportional to the square of the partial pressure of H_2O_2 at a constant partial pressure of water vapour; water vapour was found to retard the reaction slightly.

5. The reaction has been found to be a surface reaction of an unusual type, the equation governing the rate of reaction being:

$$-\frac{d[H_2O_2]}{dt} = \frac{k[H_2O_2]^2}{(1 + b'[H_2O])^2}$$

$\underline{k}$ and $\underline{b}'$ in the experiments under consideration having the values 0.06 and 0.15 respectively, when the rates were expressed in millimetres per minute. This equation has also been derived theoretically from equilibrium considerations.

6. Periodic variations have been observed in decomposition curves for experiments performed in the presence of high pressures (about 10 mm.) of water vapour. Possible reasons for this behaviour have been discussed.

7. The effect, on the decomposition, of various gases has been investigated; oxygen and nitrogen, at higher pressures (above about 10 mm.), retard the reaction to approximately the same extent, as would be expected from diffusion theory.

8. The apparent heat of activation of the reaction has been found to be approximately 7500 cals. over the temperature range 60 - 140°C, but much smaller (about 3800 cals.) over the range 15 - 60°C.

9. An attempt has been made to evaluate an equation giving the reaction velocity for a reaction of this type, as derived from the theory of absolute reaction rates. The velocity so determined was found to be 9.7×10^{12} molecules H_2O_2 $cm.^{-2}$ $sec.^{-1}$, in good agreement with the experimental value of 15.9×10^{12} molecules H_2O_2 $cm.^{-2}$ $sec.^{-1}$

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REFERENCES.

1. Thénard, Ann. Chim. Phys., (2) 8, 306, (1818); "Traité de Chimie", 4me. éd. 2, 41. Principal Papers - Ann. Chim. Phys., (2) 9, 51, 94, 314, (1818); (2) 11, 208, (1819); (2) 50, 80, (1832); loc. cit. in 5.
2. Maass and Hatcher, J.A.C.S., 42, 2548, (1920).
3. Kilpatrick, Reiff and Rice, ibid., 48, 3019, (1926).
4. Fehér, Ber., 72B, 1789, (1939).
5. Thénard, Ann. Chim. Phys., (2) 9, 441, (1818); (2) 10, 114, 335, (1819); (2) 11, 85, (1819).
6. See e.g. Brodie, Chem. Soc. Quart. J., 4, 194, (1851); Pelouze and Fremy, "Traité de Chimie Générale", 2me. éd., 1, 231, (1854).
7. Watts' Dictionary of Chemistry, 1st. Ed., 3, 196, (1865).
8. ibid., 1st. Supplement, 719, (1872).
9. Schöne, Ber., 11, 482, 561, 874, (1878).
10. Schöne, Annalen, 196, 239, (1879); Brodie, Phil. Trans., 162, ii, 454, (1872); Leeds, J.A.C.S., 2, 34, 147, (1880).
11. Schöne, Ber., 13, 623, (1880); Berthelot, Compt. rend., 90, 334, (1880).
12. Schöne, Annalen, 197, 137, (1879); Berthelot, Compt. rend., 95, 8, (1882).
13. Berthelot, Bull. Soc. chim., (2) 34, 78, (1880).
14. (a) Brodie, Phil. Trans., 140, ii, 779, (1850); (b) Schöne, Z. anal. Chem., 18, 133, (1879); (c) Bourgougnon, J.A.C.S., 11, 94, (1889).

15. Rice, J.A.C.S., 48, 2099, (1926).

16. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 1, 933, (1922).

17. Urey, Dawsey and Rice, J.A.C.S., 51, 1371, (1929).

18. Allmand and Style, J.C.S., 1930, 596, 606.

19. Heidt, J.A.C.S., 54, 2840, (1932).

20. Kornfeld, Z. wiss. Phot., 21, 66, (1921).

21. Kornfeld, Z. physikal. Chem., B29, 205, (1935).

22. Haber and Weiss, Naturwiss., 20, 948, (1932); Proc. Roy. Soc., A147, 332, (1934).

23. Blaedel, Ogg and Leighton, J.A.C.S., 64, 2499, (1942).

24. (a) Bredig and Weinmayr, Z. physikal. Chem., 42, 601, (1903); (b) Hedges and Myers, "The Problem of Physico-chemical Periodicity", 53, (1926).

25. (a) Schwarz and Friedrich, Ber., 55B, 1040, (1922); (b) Kailan, ibid., 55B, 2492, (1922); Schwarz and Friedrich, ibid., 55B, 2494, (1922).

26. Inter alia - Maass and Hatcher, loc. cit. in 2; Maass and Herzberg, J.A.C.S., 42, 2569, (1920); Maass and Hiebert, ibid., 46, 2693, (1924); Cuthbertson, Matheson and Maass, ibid., 50, 1120, (1928); Cuthbertson and Maass, ibid., 52, 489, (1930); Butler and Maass, ibid., 52, 2184, (1930); Linton and Maass, Canadian J. Res., 7, 81, (1932); Giguère and Maass, ibid., 18B, 181, (1940).

27. Hinshelwood and Prichard, J.C.S., 123, 2726, (1923).

28. Elder and Rideal, Trans. Faraday Soc., 23, 545, (1927).

29. Kistiakowsky and Rosenberg, J.A.C.S., 59, 422, (1937).

30. Deville, "Leçons sur la dissociation", Paris, 307, (1864).

31. Warburg, Ber. deut. phys. Ges., 17, 194, (1915).

32. Meidinger, Annalen, 88, 57, (1853); Bunsen, Pogg. Ann., 91, 621, (1854); Schönbein, ibid., 65, 161, (1845); Le Blanc, Compt. rend., 75, 170, (1872).

33. Nernst, Z. Elektrochem., 11, 710, (1905).

34. Fischer and Ringe, Ber., 41, 945, (1908).

35. Mellor, loc. cit. in 16, p. 924.

36. M. Traube, Ber., 18, 1890, (1885).

37. Inter alia - von Elbe and Lewis, J. Chem. Physics, 10, 366, (1942); Bates and Taylor, J.A.C.S., 49, 2438, (1927).

38. M. Traube, Ber., 26, 1471, (1893).

39. Walton and Filson, J.A.C.S., 54, 3228, (1932).

40. Hurd and Puterbaugh, ibid., 52, 950, (1930).

41. Pietsch and Adolph, Dtsch. Reichs-Pat. 241702; D. R.-P. 243366; D. R.-P. 256148; D. R.-P. 293087.

42. Ephraim's Inorganic Chemistry, English Translation by Thorne and Roberts, 4th. Ed., 407, (1943).

43. Fehér, Ber., 72B, 1778, (1939).

44. Linton and Maass, loc. cit. in 26.

45. Butler and Maass, loc. cit. in 26.

46. Cuthbertson and Maass, loc. cit. in 26.

47. Theilacker, Z. physikal. Chem., B20, 142, (1933).

48. Penney and Sutherland, Trans. Faraday Soc., 30, 898, (1934).

49. Venkateswaran, Phil. Mag., iv, 15, 263, (1933); Nature, 127, 406, (1931).

50. Simon and Fehér, Z. Elektrochem., 41, 290, (1935).

51. (a) Fehér and Klötzer, ibid., 41, 850, (1935); 43, 822, (1937);

51. (b) Natta and Rigamonti, Gazz. chim. ital., 66, 762, (1936).

52. Randall, Proc. Roy. Soc., A159, 83, (1937).

53. Lu, Hughes and Giguère, J.A.C.S., 63, 1507, (1941).

54. Giguère and Schomaker, ibid., 65, 2025, (1943).

55. Zumwalt and Giguère, J. Chem. Physics, 9, 458, (1941).

56. Geib and Harteck, Ber., 65B, 1551, (1932).

57. Taylor, J.A.C.S., 48, 2840, (1926) gives references to this date; see also Bates and Salley, ibid., 55, 110, (1933), and reference 37.

58. Kistiakowsky, "Photochemical Processes", New York, 173, (1928); see also Bonhoeffer and Harteck, "Grundlagen der Photochemie", Leipzig, (1933).

59. Kornfeld, loc. cit. in 20; see also Henri and Wurmser, Compt. rend., 156, 1012, (1913); 157, 126, 284, (1913).

60. Griffith and McKeown, "Photoprocesses, etc.", 459 - 461, (1929).

61. Rice and Kilpatrick, J. Physical Chem., 31, 1507, (1927).

62. Pana, Trans. Faraday Soc., 24, 486, (1928).

63. Wright and Rideal, ibid., 24, 530, (1928).

64. Jeu and Alyea, J.A.C.S., 55, 575, (1933).

65. Lemoine, J. Chim. phys., 12, 1, (1914).

66. Clayton, Trans. Faraday Soc., 11, 164, (1915).

67. Rice and Reiff, J. Physical Chem., 31, 1352, (1927).

68. Williams, Trans. Faraday Soc., 24, 245, (1928).

69. Wright, ibid., 24, 539, (1928).

70. Giguère and Maass, Canadian J. Res., 18B, 84, (1940).

71. von Elbe and Lewis, loc. cit. in 37.

72. Giguère and Maass, loc. cit. in 26.

73. Fowler and Bright, J. Res. Nat. Bur. Stand., 15, 493, (1935).

74. Cumming and Kay, "Quantitative Chemical Analysis", 8th. Ed., 106, (1942).

75. Farkas and Melville, "Experimental Methods in Gas Reactions", 161, (1939).

76. Maass and Hiebert, loc. cit. in 26.

77. Maass and Herzberg, loc. cit. in 26.

78. Maass and Hatcher, loc. cit. in 2, p.2568; Mellor, loc. cit. in 16, p.936.

79. Ritchie, Proc. Roy. Soc., A146, 828, (1934); ibid., A146, 848, (1934); Ritchie and Taylor, ibid., A180, 423, (1942).

80. See e.g. Oldenberg and Sommers, J. Chem. Physics, 9, 432, (1941).

81. Bredig and von Berneck, Z. physikal. Chem., 31, 289, (1900); Dyer and Dale, Proc. Chem. Soc., 29, 55, (1913).

82. Hinshelwood, "The Kinetics of Chemical Change", 178 - 233, (1940); Glasstone, "Recent Advances in Physical Chemistry", 3rd. Ed., 398 ff., (1936).

83. Glasstone, Laidler and Eyring, " The Theory of Rate Processes", New York, 339 ff., (1941).

84. Bachman and Taylor, J. Physical Chem., 33, 447, (1929).

85. Hedges and Myers, loc. cit. in 24, pp. 14 - 15.

86. McBain, "The Sorption of Gases and Vapours by Solids", 229, 331, 495, (1932); Mee, "Physical Chemistry", 2nd. Ed., 425, (1939).

87. Melville and Ludlam, Proc. Roy. Soc., A132, 108, (1932); also Ritchie and Taylor, loc. cit. in 79.

88. Smith, J. Chem. Physics, 11, 110, (1943).